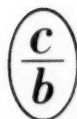


Volume 19 Number 6
June 1949

JOURNAL OF
GENERAL
CHEMISTRY
of the USSR

ЖУРНАЛ ОБЩЕЙ ХИМИИ
(ZHURNAL OBSHCHEI KHIMII)

TRANSLATED FROM RUSSIAN



CONSULTANTS BUREAU, NEW YORK

THE JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Vol. 19, 1949

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THE JOURNAL OF GENERAL CHEMISTRY OF THE U. S. S. R..

Vol., 19 (1949)

No., 6 (June)

Publication of the Academy of Sciences of the U. S. S. R.

IN ENGLISH TRANSLATION

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CONSULTANTS BUREAU

153 West 33 Street
New York 1, N. Y.

Printed in the United States of America.

Annual Subscription \$95.00. Single issue \$12.00

ON THE RATIONAL REPRESENTATION OF THE PERIODIC SYSTEM OF THE ELEMENTS

A. E. Shtandiyel

In the present note a method of constructing the table is proposed which, in the opinion of the author, unites the requirements for simplicity and convenience, and at the same time also gives the electronic structure of the elements.

In the table, as opposed to the generally accepted tradition, the elements are placed on horizontal lines from the bottom up. This method of constructing the table corresponds to the gradual increase in complication of the atom, and to the energy levels given by the usual scheme.

Every horizontal line corresponds to a definite increase of the level, shown at the left side of the table. The levels are distributed, not in the order of their principal and secondary quantum numbers, but in the order in which they are actually filled with respect to their energy values. This sort of distribution permits one to see at a glance the process of formation of the periods, and in addition, agrees with the usual distribution of elements according to adjacent horizontal lines. In order to preserve the basic principle of gradual filling of one or another level, the levels 5d and 6d are written twice, as they are filled in two different ways.

In the case of lanthanum, 5d has a single electron, and then 4f is built up through the rare earths; finally, the filling up of the 5d level is resumed with Hf. Analogous relations are suggested later on for the group Ac-Pu.

The rare earths are often excluded from the table without sufficient cause (most often in order to shorten the number of vertical groups).

In accordance with the latest investigations of the uranium group, and the establishment of analogies between this group and the rare earths, there is an imperative demand for the inclusion of both groups in corresponding places in the table.

All the similar elements, in our table, as always, fall in a single vertical group. The elements Cu, Zn, Ag, Cd, Au and Hg are written in series after the triads Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt at the right, in accordance with their isolation from the alkaline and alkaline earth elements. With these elements, the building of the d-levels is completed, and they naturally complete the horizontal groups of ten elements.

In order to avoid the unnecessary complication of the system, the elements Fe, Ru, Os; Co, Rh, Ir; Ni, Pd, Pt have been assigned to three places, despite a certain possibility of difference in electronic configurations.

At the top of the table there is given, for every vertical group, the structure of the two last levels in the series, distributed according to the quantum numbers n and l ; for the rare earths and the uranium group, there is shown the configuration of all the last levels, beginning with the increased level.

The series of levels according to increasing n and l is given in the footnote to the table, as it is necessary in order to determine the complete electronic

configuration of the atom in the customary form. The distribution of levels according to n and l generally has a rather provisional character, as during the process there is a failure to observe the principle of gradual increase of the energy of the electronic condition, a principle which plays a basic role in the genesis of the system of elements. However, taking into account the usual terminology, as well as the actual behavior of the atoms during chemical reactions, the structure of the inner levels is given precisely by the indicated arrangement.

The proposed table permits one almost automatically to determine the complete electronic configuration of any atom. For this purpose it is sufficient to utilize the numbers written at the left in the columns 'increasing level' and 'number of places in level', to be able to write out all those levels which are already filled in the case of the given elements, and to complete the writing of the structure of the final level; the same results can be attained by simply reading the place of the element in the corresponding horizontal series, or by glancing at the column 'structure of outer levels'. If desirable, the configuration can be written in the usual form according to increasing n and l at the same time as the levels are written out, or with the aid of the series presented in the footnote.

The number of unpaired electrons, which is important for quantum theory, is easily found according to Hund's rule from the number of doublet nuclei and the configurations of the final levels, but for convenience, the number of unpaired electrons is shown at the top of the table for every vertical group; at the same time, the condition of the unpaired electrons is also given.

Received by Editor
November 11, 1947.

PERIODIC SYSTEM OF THE ELEMENTS

[illegible]

The two final levels in the series, distributed according to increasing quantum numbers n and l , refer to the external levels.

1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d, 5f, (5g), 6s, 6p, 6d, (6f), (6g), (6h), 7s.

The levels in parentheses are unfilled.

For the rare earths and the uranium group, the last five levels are shown, beginning with increased level f.

PERIODIC SYSTEM OF THE ELEMENTS

[illegible]

numbers n and l , refer to the external levels.

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firming with increased level f.

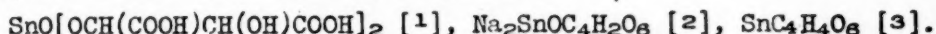
THE REACTIONS OF TIN SALTS

WITH THE TARTRATES OF THE ALKALINE METALS

V. K. Zolotukhin

Lvov State University

The reactions of tin salts with the tartrates of the alkaline metals, as well as the tin tartrates themselves, have been insufficiently studied, despite the fact that this reaction has both practical and theoretical interest. It is known from the literature that with tartaric acid and the tartrates of the alkaline metals, tin forms the following compounds:



From the first two formulas, it is evident that the tartrate compounds of tetravalent tin are formed by means of the substitution by SnO^{++} of the hydrogen of the hydroxyl group, and that the reaction for obtaining them must be accompanied by the formation of acid. From the third formula it is evident that the reaction for the formation of the tartrate of bivalent tin is not accompanied by an increase in acidity. The purpose of the present work was to study the acid balance of the reaction of tin salts with the tartrates of the alkaline metals and the stability of the tartaric acid compounds of tin, as well as to determine in what relative quantities the salts of tin and the tartrates of the alkaline metals react to form stable soluble tartrate compounds of tin.

I. Study of the Reaction of Tetravalent Tin

The work was performed with chemically pure stannic chloride and sodium tartrate.

The acid balance of the reaction of stannic chloride with sodium tartrate was determined in the following manner: a definite volume of the solution of stannic chloride was used, and an excess of a solution of sodium tartrate was added.

By means of titration with alkali, using phenolphthalein, the amount of free acid formed in the reaction was determined. The amount of free acid in the solution of stannic chloride was calculated from the difference between the amount of total (free plus bound) acid, determined either iodometrically (4) or acidimetrically after complete hydrolysis of the salt (5), and the amount of acid bound to the tin.

The experiments performed showed that during the reaction of stannic chloride with sodium tartrate, four equivalents of acid are formed for each molecule of stannic chloride, in accordance with its tetravalent condition. Results are given in Table 1. Titration with thymolphthalein gives results similar to those of titration with phenolphthalein. Thus, in titrating with phenolphthalein, on an average, 29.58 ml of 0.1 N NaOH were consumed; with thymolphthalein, 29.72 ml.

An excess of alkaline metal tartrate, as the experiments showed, did not influence the acid balance of the reaction.

Experiments carried out with the β compounds of tetravalent tin, obtained by the methods of Kuznetsov, showed that these react with sodium tartrate like

the α -compounds. Consequently, the amount of acid determined in the solution of the tin compound (IV) by means of sodium tartrate and iodometry, agrees satisfactorily. Thus, the general acidity was determined as the average of 4 experiments: iodometric method, 7.54 equiv./mg., tartratometric, 7.65 equiv./mg.

During the mixing of the solutions of alkaline metal tartrate and stannic chloride or during the titration of the mixture with alkali, there may be formed acid-soluble precipitates of tin tartrates. Near the equivalent point in the titration with alkali, using phenolphthalein, they however, go into solution, obviously as the result of the transformation of the tin tartrates into another form. In connection with this, work was undertaken on the determination of the

Table 1

No. of expt.	SnCl ₄ taken, equiv. to mg. SnO ₂	Content of free acid in volume taken (in ml 0.1 N solution)	Total acid determined after reaction (in ml 0.1 N solution)	Quantity of acid formed during reaction (in ml 0.1 N solu.)	Percent titrated acid compared to theoretical
1	84.90	48.20	70.86	22.66	100.54
2	84.90	48.22	70.90	22.68	100.63
3	84.90	48.20	70.83	22.63	100.43
4	42.45	24.10	35.43	11.33	100.54
5	42.45	24.12	35.42	11.30	100.31
6	42.45	24.09	35.39	11.30	100.31
7	42.45	24.10	35.37	11.27	100.17
Average					100.42

relative quantities of SnCl₄ and Na₂C₄H₄O₆ reacting with each other: titrated solutions of stannic chloride and sodium tartrate were mixed in different relative proportions and titrated with alkali and phenolphthalein with subsequent retitration, independent of whether or not a precipitate formed, either during the mixing or during the process of titration. Solutions of SnCl₄ and Na₂C₄H₄O₆ were used in concentrations of 0.1 and 1.0 N. Stannic chloride and sodium tartrate were mixed in molecular ratios: 4:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4, 1:6, 1:8, 1:12, 1:20. In every case, except for the first, the titrated mixtures of solutions of stannic chloride and sodium tartrate were transparent at the equivalent point (by phenolphthalein), although with the 3:1 and 2:1 ratios they clouded comparatively quickly.

With the following five ratios: 1:4, 1:6, 1:8, 1:12, 1:20, no formation of precipitate could be observed in the process of titration with phenolphthalein down to the equivalent point. In a medium alkaline to phenolphthalein the tartrate compound of tin (IV) was unstable, and a precipitate separated out from its solutions if the quantity of sodium tartrate did not surpass four times the relative quantity of stannic chloride (in moles).

The stability of the tartrate compound, in the neutral as well as in the alkaline region, depends upon the temperature, decreasing as the latter increases. It is interesting to observe that the transparent solutions of the tin tartrate compound, neutral to phenolphthalein, obtained by the reaction of stannic chloride with sodium tartrate in relative molar quantities of 3:1, 2:1, 1:1, and 1:2, cloud up under the action of HCl or KCl. This testifies to the fact that the tin tartrates may exist in the form of colloid solutions, and coagulate under the action of potassium chloride.

Table 2

No. of expt.	rel. quans. (in moles.)		No. of acid equivs. formed during reac- tion with 1 mol SnCl_4	behavior of acid solutions of tin tartrate toward:			Behavior of sols. of tin tartrate neut. to phenolphthalein toward.					
	SnCl_4	$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$		$\text{K}_4[\text{Fe}(\text{CN})_6]$	Na_2HPO_4	H_2S	Heat	1 N. NaOH (2 or 3 drops per 2 or 3 ml. tartrate)		$\text{K}_4[\text{Fe}(\text{CN})_6]$	Na_2HPO_4	H_2S
								in cold	upon heating			
1	4	1	4									
2	3	1	4	p	p	p	p	p	p	p	p	p
3	2	1	4	p	p	p	p	p	p	p	p	p
4	1	1	4	p	p	p	p	g. p.	p	n. p.	n. p.	p
5	1	2	4	p	p	p	p	g. p.	p	n. p.	n. p.	p
6	1	3	4	p	p	p	n. p.	n. p.	p	n. p.	n. p.	p
7	1	4	4	s. p.	n. p.	p	n. p.	n. p.	s. p.	n. p.	n. p.	p
8	1	6	4	n. p.	n. p.	p	n. p.	n. p.	n. p.	n. p.	n. p.	p
9	1	8	4	n. p.	n. p.	p	n. p.	n. p.	n. p.	n. p.	n. p.	p
10	1	12	4	n. p.	n. p.	p	n. p.	n. p.	n. p.	n. p.	n. p.	p
11	1	20	4	n. p.	n. p.	p	n. p.	n. p.	n. p.	n. p.	n. p.	p

p - precipitate
n.p. - no precipitate

g.p. - gradual precipitate
s.p. - slow precipitate

Table 4

No. of expt.	rel. quants. (in moles)		Upon addi- tion of $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ to weakly acid solu. of SnCl_2 .	At equiv. points accord- ing to phenol- phthalein.	Vol. of NaOH con- sumed in ti- tration (in ml)	Stability of Acid Solution of tin tartrate with regard to:				Stability of tin tartrate sols. neutral to phenolphthalein with regard to:					
	SnCl_2	$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$				heat	Na_2OPH_4		Na_2S	heat	NaOH (3 to 5 drops 1.0 N to 1 or 2 ml tartrate)		$\text{K}_2[\text{Fe}(\text{CN})_6]$	Na_2HPO_4	Na_2S
							cold	hot			cold	hot			
1	2	1	p	s.c.	5.28										
2	1	1	p	c.	5.25	n.p.	p		p						
3	1	2	p	c.	5.26	n.p.	p		p						
4	1	3	n.p.	w.c.	5.24	n.p.	p		p		p				p
5	1	4	n.p.	t	5.22	n.p.	p		p	n.p.	p		n.p.	n.p.	p
6	1	6	n.p.	t	5.22	n.p.	c	p	p	n.p.	n.p.	n.p.	n.p.	n.p.	p
7	1	8	n.p.	t	5.20	n.p.	t	p	p	n.p.	n.p.	n.p.	n.p.	n.p.	p
8	1	10	n.p.	t	5.20	n.p.	t	p	p	n.p.	n.p.	n.p.	n.p.	n.p.	p
9	1	12	n.p.	t	5.18	n.p.	t	p	p	n.p.	n.p.	n.p.	n.p.	n.p.	p
10	1	16				n.p.	t	p	p						
11	1	24				n.p.	t	n.p.	p						

p-precipitate
n.p. no precipitate

t-transparent
c-cloudy

s.c-strongly cloudy
w.c.-weakly cloudy

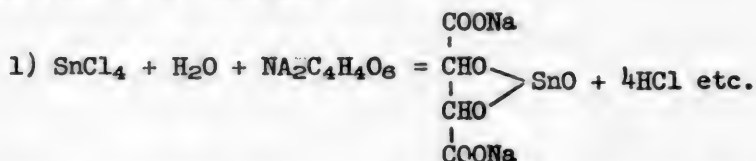
The tartrate compounds of tin were tested for their stability toward $K_4Fe(CN)_6$, Na_2HPO_4 , H_2S , $NaOH$, and heat. Results are presented in Table 2.

The decomposition of the tartrate compounds of tin (IV) by hydrogen sulfide was observed not only with the amounts of sodium tartrate shown in Table 2, but even in the presence of a much greater excess, up to 70 fold (a still greater excess was not used). As is evident from this table, the tartrate compounds of tin neutral to phenolphthalein were more stable than when acidified, a fact which may be related to the change in its condition in the passage from acid medium to alkaline; therefore it became of interest to make clear whether the acid was formed all at once during the mixing of stannic chloride with sodium tartrate, or gradually in the process of titration as a result of the further substitution of the hydrogen of the hydroxyl group by ions of tin.

For this purpose, the precipitates of tin tartrate were filtered after the free acid had been reduced to 0.05 N, and the quantity of acid determined in the filtrate; this acid had been formed in the reaction between stannic chloride and sodium tartrate. It showed exactly four equivalents, thus testifying to the substitution of the hydrogen of the hydroxyl group by the tin ions even in a weakly acid medium.

As with the increase of the relative amounts of sodium tartrate, the stability of the tin tartrate compounds increases (Table 2), we must assume that with the different molecular ratios of stannic chloride and alkaline metal tartrate, different tin tartrate compounds are formed, whose composition may be reflected by such formulas as those of Table 3.

The equations for the formation of the indicated tartrate compounds of tetravalent tin will be of this sort:



The indicated formulas correspond to the experimental facts: 1) the formation of four equivalents of acid per molecule of SnCl_4 , and 2) the increase in the stability of the tin tartrate compounds with an increase in the molecular ratio of sodium tartrate per mole stannic chloride.

The formation of a precipitate upon heating the solutions of several of the tin tartrates (Table 2) is, obviously, a result of the hydrolysis of these tartrates.

II. Study of the Reaction of Bivalent Tin

In the literature (3) there is a reference to a tartrate compound of tin with the composition $\text{SnC}_4\text{H}_4\text{O}_6$. As is evident from the formula, the tin tartrate is formed by the substitution of the tin ion for the hydrogen of the carboxyl group. Experiments conducted by us showed that during the reaction of salts of bivalent tin with the alkaline metal tartrates, the formation of acid was observed. This gave cause to suppose that the ions of bivalent tin substituted the hydrogen of the hydroxyl group of the tartrate. In connection with this, it was of interest to study the acid balance of the reaction $\text{Sn}^{++} + \text{C}_4\text{H}_6\text{O}_6$ and the stability of the tartrate compounds of tin (II) with regard to various reagents. This work was carried out with solutions of stannous chloride and sodium tartrate of 0.1 N and 1.0 N concentration. The figures of Table 4 were obtained by work with 1.0 N concentrations of SnCl_2 and $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$.

The titre of the stannous chloride was performed iodometrically. The concentration of free acid in the solution of stannous chloride was determined by the difference between the total acidity, found iodometrically (4), and the acid bound to the SnCl_2 .

The acid balance of the reaction between stannous chloride and sodium tartrate was determined in this manner: to a definite volume of SnCl_2 solution there was added a definite volume of a solution of $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ neutral to phenolphthalein, and the solution was titrated with caustic soda and phenolphthalein. The acid (after mixing SnCl_2 and $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$) and neutral solutions of tin tartrate obtained were tested for their stability to NaOH , Na_2HPO_4 , $\text{K}_3\text{Fe}(\text{CN})_6$ and Na_2S (Table 3):

Table 3

Molecular ratios SnCl_4 and $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$	Formulas	Molecular ratios $\text{SnCl}_4 : \text{Na}_2\text{C}_4\text{H}_4\text{O}_6$	Formulas
2:1	$ \begin{array}{c} \text{COONa} \\ \\ \text{CHO}-\text{SnO} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{O} \\ \\ \text{CHO}-\text{SnO} \\ \\ \text{COONa} \end{array} $	1:3	$ \begin{array}{ccc} \text{COONa} & & \text{NaOOC} \\ & & \\ \text{CHO}-\text{SnO}-\text{OHC} & & \\ & \diagdown \quad \diagup & \\ \text{CHOH} & & \text{HOHC} \\ & & \\ \text{COONa} & & \text{NaOOC} \\ & \diagup \quad \diagdown & \\ & \text{COONaCHOHCHOHCOONa} & \end{array} $
1:1	$ \begin{array}{c} \text{COONa} \\ \\ \text{CHO} \quad \diagdown \quad \text{SnO} \\ \\ \text{CHO} \\ \\ \text{COONa} \end{array} $	1:4 etc.	Similar to the foregoing, but with an increased number of coordinated molecules of tartrate to 1 tin atom, and so forth.
1:2	$ \begin{array}{ccc} \text{COONa} & & \text{NaOOC} \\ & & \\ \text{CHO}-\text{SnO}-\text{OHC} & & \\ & \diagdown \quad \diagup & \\ \text{CHOH} & & \text{HOHC} \\ & & \\ \text{COONa} & & \text{NaOO-C} \end{array} $		

During the addition of sodium tartrate to the strongly acid solution of stannous chloride, no formation of a tin tartrate precipitate is observed, with any of the different ratios of stannous chloride and sodium tartrate used. With weak acidity of the solution, a white flocculent quickly precipitating tin tartrate settles out, if the molecular quantity of sodium tartrate exceeds the molecular quantity of stannous chloride by less than three times. With a three- and more fold quantity of sodium tartrate, no precipitate is formed. It is necessary to observe that from 0.1 N solutions of stannous chloride and with a fourfold quantity of sodium tartrate there separates a precipitate of tin tartrate (probably basic) which upon titration with alkali in the presence of phenolphthalein dissolves as the equivalent point is approached. As is evident from Table 4 the stability of the tin tartrates with regard to NaOH , Na_2HPO_4 and $\text{K}_3\text{Fe}(\text{CN})_6$ increases along with an increase in the relative molecular quantities of sodium tartrate. With a 1:6 ratio the neutral solutions of tin tartrate obtained are not decomposed by the indicated reagents either cold or hot. With regard to the action of Na_2S upon tin tartrates, this reagent throws out of its solutions a precipitate of tin sulfide, even in the presence of a very great relative quantity of sodium tartrate up to a ratio of 30 fold in neutral solution and 75 fold in

acid solution (the experiments were not continued with greater quantities of sodium tartrate).

The determination of the acid formed during the reaction of stannous chloride with sodium tartrate by titration with phenolphthalein indicator (also with thymolphthalein) shows that the acid is formed in a quantity of $\frac{3}{4}$ of the theoretical. Thus, for example, in the reaction of sodium tartrate with 6.13 ml of 0.1 N solution of stannous chloride, 4.64 ml of 0.1 N acid are formed in solution, corresponding to 75.7% of the theoretical. To explain the kinetics of the reaction, it was necessary to decide whether this acid was formed all at once during the mixing of the reagent solutions or gradually in the process of titration with alkali by means of the further substitution of the hydrogen of the hydroxyl group by ions of bivalent tin.

With this object in view, the amount of acid was determined in the filtrate from the precipitate of tin tartrate. The precipitates of tin tartrate were obtained either directly by the action of sodium tartrate upon 0.05 N acidic solutions of stannous chloride, or upon dry $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. In every case, the quantity of tartrate of bivalent tin remaining in solution and the quantity of tin oxidized during the experiment were determined iodometrically, account being taken of the quantity of acid formed during the reaction.

The experiments were conducted with the relative molar quantities of stannous chloride and sodium tartrate expressed by the ratios 1:1, 1:2, 1:4 (with higher ratios of sodium tartrate, precipitates of tin tartrates were not formed). These experiments showed that with relative quantities of stannous chloride and sodium tartrate 1:1, acid was formed in an amount of 50% of the theoretical, with 1:2, 54%, with 1:4, 58% of the theoretical.

With relative quantities 1:6, 1:8, 1:10 and 1:12, the determination of acid by titration with alkali and phenolphthalein indicator was not accompanied by the formation of precipitates of tin tartrates all the way to the equivalent point, and gave 75% of the theoretical amount.

Table 5

Molecular ratios		Formula of tin tartrate formed in:	
SnCl_2	$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$	Weakly acid medium	medium neutral to phenolphthalein
1	1	$\begin{array}{c} \text{COONa} \\ \\ \text{CHOH} \\ \\ \text{CHO} \text{---} \text{Sn} \\ \\ \text{COO} \end{array} \quad \text{or} \quad \begin{array}{c} \text{COONa} \\ \\ \text{CHOH} \\ \\ \text{CHOH} \\ \\ \text{COOSn(OH)} \end{array}$	$\begin{array}{c} \text{COONa} \qquad \qquad \text{NaOOC} \\ \qquad \qquad \qquad \\ \text{CHO} \text{---} \text{Sn} \text{---} \text{OHC} \\ \qquad \qquad \qquad \\ \text{CHO} \text{---} \text{Sn} \text{---} \text{HOHC} \\ \qquad \qquad \qquad \\ \text{COO} \qquad \qquad \text{NaOOC} \end{array}$
1	2	$\begin{array}{c} \text{COONa} \qquad \qquad \text{NaOOC} \\ \qquad \qquad \qquad \\ \text{CHOH} \qquad \qquad \text{HOHC} \\ \qquad \qquad \qquad \\ \text{CHO} \text{---} \text{Sn} \text{---} \text{HOHC} \\ \qquad \qquad \qquad \\ \text{COO} \qquad \qquad \text{NaOOC} \end{array}$	$\begin{array}{c} \text{COONaCHOHCHOHCOONa} \\ \qquad \qquad \qquad \\ \text{COONa} \qquad \qquad \text{NaOOC} \\ \qquad \qquad \qquad \\ \text{CHO} \text{---} \text{Sn} \text{---} \text{OHC} \\ \qquad \qquad \qquad \\ \text{CHO} \text{---} \text{Sn} \text{---} \text{HOHC} \\ \qquad \qquad \qquad \\ \text{COO} \qquad \qquad \text{NaOOC} \\ \text{COONaCHOHCHOHCOONa} \end{array}$
1 etc.	3	Similar to the above, but with a greater number of coordinated molecules of tartrate to 1, etc.	

Proceeding from the data on the acid balance of the reaction and the fact of increased stability of the tartrate compounds of bivalent tin with an increase in the relative molar quantities of sodium tartrate entering into the reaction with tin chloride, we consider as probable the formation of such complex tartrates of bivalent tin as in Table 5.

The study of the properties and composition of tartrate compounds of tin (II, IV) is being continued.

SUMMARY

1. It has been confirmed that during the reaction of salts of tetravalent tin with tartrates of alkaline metals, acid is formed by means of the substitution of the hydrogen of hydroxyl groups by tin ions.

2. It has been confirmed that an excess of the alkaline metal tartrate does not influence the acid balance of the reaction with salts of tetravalent tin.

3. It has been shown that with relative molar quantities of stannous chloride and alkaline metal tartrate ranging from 3:1 to 1:20 four equivalents of acid are always separated.

4. During the reaction of salts of bivalent tin with the tartrates of the alkaline metals in weakly acid and neutral (to phenolphthalein) solutions, acid is also separated as a result of the substitution of the hydrogen of the hydroxyl group by Sn^{++} , in quantities from 50% to 75% of the theoretical, the amount depending upon the relative quantities of the reagents and the pH of the solution.

With an increase of these relative quantities up to 1:12 and a pH up to 10 (titration with thymolphthalein) the formation of acid beyond 75% of the theoretical was not observed. This last fact is probably related to the insufficiently strong polarizing properties of Sn^{++} .

The formation of the $\text{SnC}_4\text{H}_4\text{O}_8$ described in the literature is possible only in strongly acid medium.

5. The stability of the tin tartrates toward the different reagents increases with an increase in the relative quantities of alkaline metal tartrate.

6. On the basis of the study of the acid balance of the reaction of tin salts with the tartrates of alkaline metals and the stability of the tin tartrates formed during this reaction, there is proposed a probable formula of the tartrates of bivalent and tetravalent tin.

7. The reaction of the salts of tetravalent tin with the tartrates of the alkaline metals can be utilized for the quantitative determination of tin by using a method for the direct determination of free acid in the solutions of salts of tetravalent tin, and can also be utilized for the determination of the total amount of acid in such solutions.

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Received December 8, 1947.

COMPARATIVE ACCURACY OF THE SIMPLEST EQUATIONS FOR THE CALCULATION OF THE ENERGY OF CRYSTAL LATTICES

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Of the equations existing in the literature for the calculation of the energy of crystal lattices of ionic compounds, the most practically convenient is the one proposed in 1933 by A.F. Kapustinsky [1]

$$U = 256 \sum_n \frac{v_K \cdot v_A}{r_K + r_A} \text{ kilocal/mole} \quad (1)$$

This equation (where v_K and v_A are the valences of cations and anions, r_A and r_K their radii, according to Goldschmidt, \sum_n the number of ions in the chemical molecule of the compound) is characterized by moderate accuracy, but fairly important universality. It has therefore found wide use in all those cases where great accuracy is not required in the calculation of the values.

In 1943 A. F. Kapustinsky [2] proposed a somewhat more complicated formula of the kind:

$$U = 287.2 \sum_n \frac{v_K \cdot v_A}{r_K + r_A} \left(1 - \frac{0.345}{r_K + r_A} \right) \text{ kilocal/mole} \quad (2)$$

The complication introduced (an additional term) in the opinion of the author increases the accuracy of the results obtained.

As this conclusion did not seem to be on a completely confirmed basis, it seemed expedient to carry out a comparative evaluation of the accuracy of both equations of A.F. Kapustinsky on the most typical ionic compounds - the simplest derivatives of the metals of Groups I and II of the periodic system. In order to avoid arbitrariness in the choice of experimental material, there were utilized for this purpose the values obtained on the basis of the data of the well-known thermochemical handbook of Bichowsky and Rossini [3].

The results of the calculations are given below in Tables 1 and 2. The italicized upper figures of each cell represent the experimental values of the energy of the crystalline lattice, the figures at the left the magnitudes calculated according to equations 1 and 2, the figures at the right the discrepancies between the calculated values and the experimental, in percent.

As is shown, for example, by the data for the compounds of Ag and Cd, for compounds of cations with an 18 electron outer shell both equations are practically inapplicable. For cations of the type of an inert gas, the discrepancies are comparatively small but fluctuate quite irregularly.

A resume of the comparative accuracy of the two equations is given in Table 3. As is obvious from it, equation (2) is in general no more accurate than

Table 1
Compounds of metals of Group 1

Anion	Cation					
	Li	Na	K	Rb	Cs	Ag
F	242.5 242.6 0.0% 227.7 -6.1%	215.0 221.6 +3.0% 211.5 -1.0%	189.1 192.4 +1.7% 187.9 -0.6%	183.2 181.5 -0.9% 178.7 -2.4%	175.0 171.8 -1.8% 170.4 -2.6%	225.8 208.1 -7.8% 200.7 -11.8%
	199.9 197.7 -1.1% 192.2 -3.9%	182.7 183.5 +0.4% 180.4 -1.3%	164.3 163.0 -0.8% 162.8 -0.9%	160.3 155.1 -3.2% 155.8 -2.8%	154.9 148.0 -4.5% 149.4 -3.6%	212.7 174.1 -18.1% 172.4 -19.0%
	185.4 186.8 +0.7% 183.2 -1.2%	170.5 174.1 +2.1% 172.4 +1.1%	153.4 155.6 +1.4% 156.3 +1.9%	150.5 148.4 -1.4% 149.8 -0.5%	145.7 141.8 -2.0% 143.9 -1.2%	205.6 165.7 -19.4% 165.1 -19.7%
I	175.3 171.8 -2.0% 170.4 -2.8%	161.6 161.0 -0.4% 161.0 -0.4%	146.8 145.0 -1.2% 146.8 0.0	144.3 138.7 -3.9% 141.1 -2.2%	140.5 133.0 -5.3% 135.8 -3.3%	205.3 153.7 -25.1% 154.6 -24.7%
	693.8 713.4 +5.4% 658.7 -1.2%	615.1 667.8 +8.5% 636.8 +3.5%	553.0 579.6 +4.8% 565.6 +2.3%	540.4 546.6 +1.1% 537.9 -0.5%	526.4 517.1 -1.8% 512.8 -2.6%	718.5 626.9 -12.7% 604.3 -16.0%
	- -	526.5 564.7 +7.2% 553.1 +5.0%	509.3 500.3 -1.8% 498.2 -2.2%	466.5 475.5 +1.9% 476.5 +2.2%	452.3 453.1 +0.2% 456.6 +1.0%	638.3 535.2 -16.1% 528.2 -17.2%

Table 2
Compounds of metals of Group II

Anion	Cation					
	Be	Mg	Ca	Sr	Ba	Cd
F		691.2 727.9 +5.3% 682.1 -1.1%	621.2 642.7 +3.4% 616.9 -0.7%	582.0 590.8 +1.5% 574.8 -1.2%	546.5 556.5 +1.8% 546.3 0.0	-
	790.6 714.4 -9.6% 672.8 -15.0%	591.3 593.0 +0.3% 576.7 -2.5%	532.2 535.2 +0.5% 528.2 -0.8%	501.5 498.7 -0.6% 496.8 -0.9%	474.4 474.0 -0.1% 475.2 +0.2%	595.4 540.8 -9.1% 533.0 -10.5%
	724.8 667.8 -7.9% 636.8 -12.1%	560.7 560.6 0.0% 549.7 -2.0%	502.6 508.6 +1.2% 505.4 +0.5%	473.4 475.5 +0.4% 476.5 +1.6%	448.4 453.1 +1.0% 456.6 +1.8%	577.0 513.6 -11.0% 509.8 -11.6%
I	733.4 604.7 -17.5% 586.3 -20.1%	540.8 515.4 -4.7% 511.3 -5.5%	486.1 471.2 -3.0% 472.6 -2.8%	455.7 442.6 -2.0% 447.2 1.9%	429.8 423.1 -1.5% 429.6 0.0%	566.8 475.5 -16.1% 476.5 -15.9%
	1160.0 1233.7 +6.3% 1096.4 -5.5%	931.1 975.2 +4.7% 914.3 -1.8%	840.3 860.5 +2.4% 825.4 -1.8%	791.4 790.7 -0.1% 768.9 -2.8%	749.2 744.7 -0.6% 730.7 -2.5%	914.6 871.5 -4.7% 834.1 -8.8%
	-	788.2 812.7 +3.1% 786.9 -0.2%	723.0 731.4 +1.1% 719.4 -0.5%	684.7 680.4 -0.6% 675.8 -1.3%	648.3 646.1 -0.3% 645.9 -0.4%	805.0 739.3 -8.2% 726.2 -9.6%

equation (1). It can therefore be seen that discarding the latter for equation (2) offers no practical advantage.

Table 3
Resume of comparative results of equations

Type of compound	No. of cases	Mean square error (%)	
		From equation (1)	From equation (2)
Compounds Li - Cs	29	3.02	2.51
Compounds Be - Ba	28	4.55	5.17
Total	57	3.77	3.82

Equation (1) is especially convenient for application in the form proposed by B. V. Nekrasov [4].

$$U = 256 \frac{v_K + v_A}{r_K + r_A} \text{ kilocal/gram-equiv.}$$

The expression for the energy of crystalline lattices in kilocal per gram equivalent of material, rather than per mole, permits a direct comparison between the ions of compounds of the most different types.

SUMMARY

It has been shown that the complication proposed by A.F. Kapustinsky for his earlier equation for the calculation of the energy of crystalline lattices leads to no increase in accuracy.

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Received February 16, 1948.

THE CONTRACTION OF ACIDS AND ALCOHOLS DURING SOLUTION IN WATER AND ANOMALOUS CONTRACTION IN THE SYSTEM NITRIC ACID-WATER

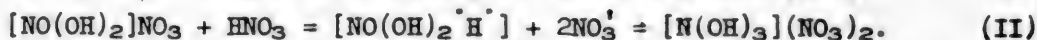
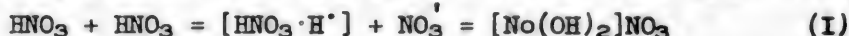
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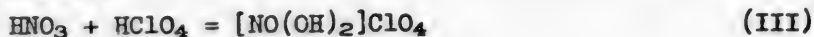
Nitric acid has for a long time attracted the attention of researchers because of the peculiarity that, in contradistinction to other acids, it possesses a high degree of electrical conductivity even in the anhydrous condition. Hantzsch [1], on the basis of general experimental observations and theoretical considerations, explained this peculiarity as being due to the fact that in pure nitric acid there exist compounds with nitrogen-containing anions as well as nitrogen-containing cations. Further, Usanovich and his co-workers [2], Lewis and Suen [3], Benford and Ingold [4], Brewin and Turner [5], Lantz [6], and many other investigators have supplied arguments based on experimental data as a result of which it is possible to reach the conclusion that every one of the nitrogen-containing ions present in nitric acid and its solutions have specific peculiarities with regard to the nitration of one or another group in chemical compounds. This circumstance lends the question of the composition and structure of nitric acid and its solution, alongside the theoretical interest, a very significant practical interest. In particular, there have now been collected [7] completely convincing arguments in favor of the conclusion that the basic nitrating agent for several very important industrially-used aromatic compounds is the cation, either in its anhydrous form NO_2^+ or in the hydrated form $\text{NO}_2 \cdot \text{H}_2\text{O} = \text{NO}(\text{OH})_2^+$.

Structural methods for the study of chemical bonds have also confirmed the considerations with regard to the presence in nitric acid of cations in the form indicated, NO_2^+ . Redlich and Nielsen [8], using the Raman spectrum, have experimentally confirmed the presence of hydroxyl bonds in individual molecules of nitric acid. Maxwell and Moseley [9] have shown that the three atoms of oxygen in the nitric acid molecule are not equivalent: in the nitro bond, the distance between the nitrogen and oxygen is 1.21 Å, in $-\text{N}-\text{O}-\text{H}$ the indicated distance is equal to 1.41 Å. Only after the addition to pure nitric acid of a certain quantity of water does there begin a process of equalization of the distances of all three atoms of oxygen from the nitrogen atom. In the nitrate ion NO_3^- thus obtained, all three atoms of oxygen are completely equivalent, the structural model is plane, and the angles $-\text{O}-\text{N}-\text{O}$ are individually equal to 120° .

Along with the ions NO_2^+ and $\text{NO}_2^+ \text{aq}$ in nitric acid and in its concentrated aqueous solutions, Hantzsch (1) assumed the presence of a second nitrogen-containing cation, specifically the doubly charged nitronium ion $\text{HN}(\text{OH})_3^{2+}$ hydro-nitracidium ion. The formation of both types of cations from the simplest molecules of nitric acid may be represented, for example, by the two following processes:



The supposition that both types of nitrogen-containing ions are present in nitric acid is confirmed by the composition of two salts: nitracidium perchlorate and hydronitracidium perchlorate:



Both synthesized salts [1] have been isolated and are not in the least explosive, but stable exothermic compounds. Similar salts have been obtained as the results of the reaction of nitric acid with several other strong acids. Usanovich [2] investigated the electrical conductivity, viscosity, and density of the binary system $\text{HNO}_3\text{--H}_2\text{SO}_4$ and found that the behavior of this system most sharply reflected the presence of the bivalent cation $\text{N}(\text{OH})_3^+$ and the univalent hydrosulfate ion HSO_4^- .

In view of the great importance of the questions discussed above, and the variety of hypotheses expressed in this regard [10], it was decided to carry out a study of the properties of the system $\text{HNO}_3\text{--H}_2\text{O}$ by several volumetric methods of investigation.

Our investigations showed that the different liquids, as they were diluted with water, showed significant contractions, which gradually, during further similar dilution with water, decreased. The initial contractions attained especially high values upon the addition of water to the strong anhydrous acids, a result which is apparently related to the extremely great energy of hydration of the hydrogen cation.

Hantzsch [1] further showed optically that parallel to the increase in the amount of water added to the nitric acid there could be observed a decrease in the number of nitronium ions present in the liquid. In the dilute solutions of nitric acid it was impossible to observe even traces of nitronium ions. In connection with this, it has just been shown [7] that the first portions of water added to the anhydrous nitric acid not only do not decrease the quantity of singly-charged nitronium ions, NO_2^+ present, but even cause a significant increase in their concentration. Only upon further dilution with water is there observed a decrease in the quantity of these singly-charged nitrogen-containing cations. When the ratio of $\text{HNO}_3\text{:H}_2\text{O}$ becomes 1:1, the nitronium cations can no longer be detected.

In the light of the facts indicated, it becomes possible, in our opinion, to suppose that the process of dilution of nitric acid with water is related to the well-studied and characteristic gradualness of electrolytic dissociation for multiply-charged ions. The first small portions of water added to the anhydrous nitric acid begin by reacting with the doubly-charged nitronium ions $\text{N}(\text{OH})_3^+$ (hydronitracidium ions), giving as products of the reaction the singly charged nitronium ions; whose number therefore increases (equation V). Only after practically complete destruction of the doubly charged nitronium ions present by the addition of excess water does the water begin to react with the singly charged ions of nitronium (equation VI).

Thus, at a ratio near $\text{HNO}_3\text{:H}_2\text{O} = 1:1$, almost all the nitronium ions, both the doubly as well as the singly charged, are destroyed, and the additional water added contributes only to the accumulation of hydroxonium ions, H_3O^+ , on the one side, and nitrate ions, NO_3^- , on the other (equation VII).

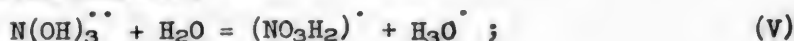
As the basic nitrating agent, as indicated above, for a series of aromatic compounds is the singly charged nitronium ion NO_2^+ and $\text{NO}_2^+\cdot\text{aq}$ [7], then in accordance with what has been said above, it is completely comprehensible that the nitrating power of nitric acid, upon dilution with water, must first increase

* $\text{NO}(\text{OH})_2^+$ (nitracidium ions).

and then diminish. Upon dilution with water to the ratio $\text{HNO}_3:\text{H}_2\text{O} = 1:1$, the nitrating ability of the solution for the group of compounds in question must be almost completely lost.

Equation (V), (VI), and (VII) illustrate what has been said.

a) Nitrating properties increase:



b) Nitrating properties weaken:



c) Nitrating properties are lost:



The correctness of equations (V) to (VII) may be confirmed by a volumetric method. The substitution of the doubly charged ions $\text{N}(\text{OH})_3^{\cdot\cdot}$ by the singly charged ions $(\text{NO}_3\text{H}_2)^{\cdot}$ and $\text{H}_3\text{O}^{\cdot}$ (equation V) must entail the weakening of the forces which act in such a way as to compress the liquid. Consequently, we may expect theoretically that the great initial contraction, which naturally takes place during the dilution of the pure liquid by the first small portions of added water in the case of the system $\text{HNO}_3 - \text{H}_2\text{O}$ must finally be very much weakened in comparison with other systems, where there is no passage of ions from one charged state to another, or where in general there are present only complete molecules which do not dissociate into ions.

In order to confirm the above statements we calculated the contraction during the process of dilution with water of those acids and alcohols for which the literature [12] gives especially accurate experimental data with regard to the specific gravities of different concentrations of solutions.

In both the tables provided (1 and 2), the first column gives the empirical formula corresponding to the chemical composition of the solution (in all cases, one mole of solvent and n moles of water). In both tables there is further given the contraction in milliliters upon mixing a mole of solution, having the composition shown in the first column, with 0.1 mole of water (= 1.80 g water); the figures of this succeeding column to a certain degree characterize the activity of the solution of the given composition with regard to the added water.

The data of Table 1 are graphically illustrated in Fig. 1. Here can be seen clearly the confirmation of the correctness of the supposition that many-charged ions are present in pure nitric acid and in its very concentrated aqueous solutions. The contraction curve of nitric acid, in the part from pure HNO_3 to $\text{HNO}_3 \cdot 0.2\text{H}_2\text{O}$, shows the sharply expressed anomaly in the process of contraction of aqueous solutions of nitric acid in comparison with the contractions of other acids and of other chemical compounds in general.

This anomaly shows that in the entire interval of gradual dilution of nitric acid from 100% to 95% (by weight) there takes place a process which weakens the contraction of the solution which is natural in such cases. In consequence of this weakened contraction, the very nature of the contraction curve becomes unusual - the addition of 1.80 g water to 63.02 g pure nitric acid at 20° (Table 2) gives a smaller contraction effect (0.19 ml) than the further addition of the same amount of water to the already diluted 95% solution of acid (0.45 ml). A completely analogous peculiarity in the contraction of concentrated aqueous solutions of nitric acid has been shown by us not only at 20°, but also at 5° and at 30° (Table 2 and Fig. 2).

The maximum contraction for all temperatures observed, as Figs. 1 and 2

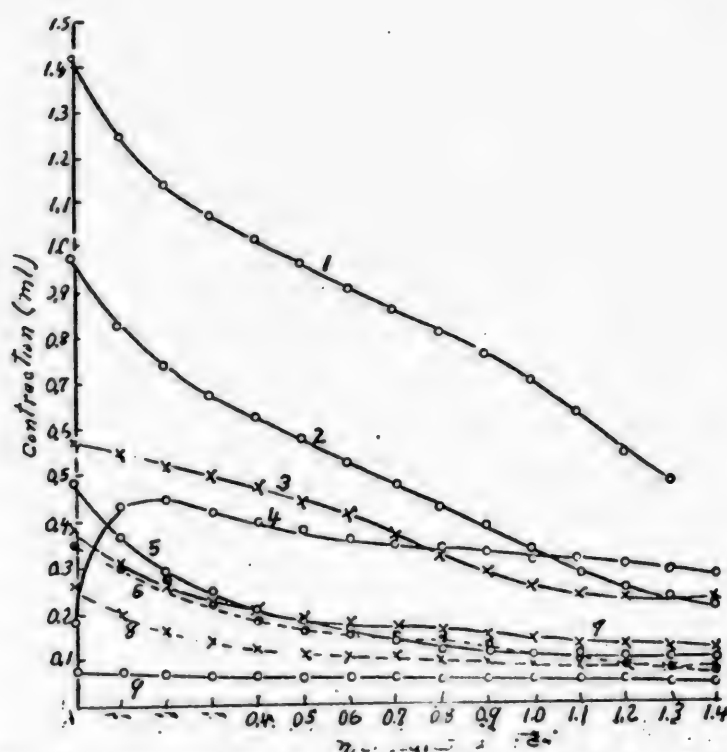


Fig. 1. Contraction in ml in reaction $A \cdot nH_2O + 0.1 H_2O$

1-Perchloric Acid; 2-sulfuric acid; 3-selenic acid; 4-nitric acid;
5-acetic acid; 6-ethyl alcohol; 7-methyl alcohol; 8-propyl alcohol;
9-glycerine.

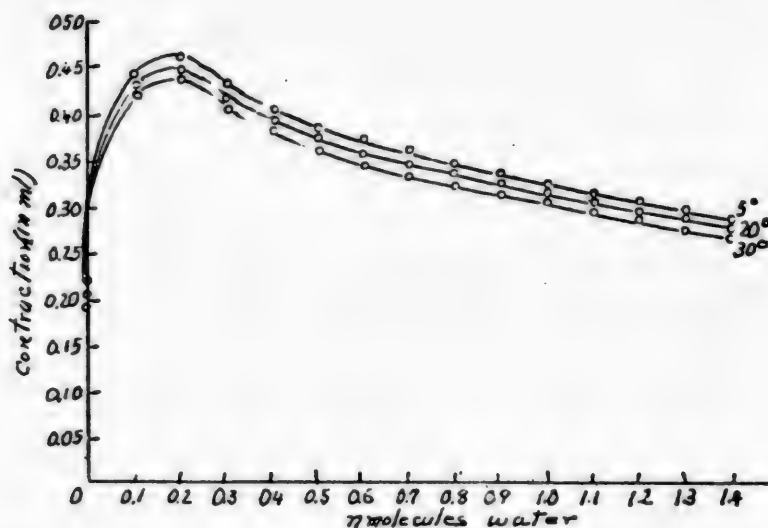
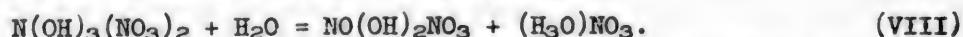


Fig. 2. Contraction in ml in reaction $HNO_3 \cdot nH_2O + 0.1 H_2O$.

show, corresponds to a 95% solution or, in other words, to a composition of $\text{HNO}_3 \cdot 0.2\text{H}_2\text{O}$. We may suppose that this composition already corresponds to only a small quantity of many-charged nitronium cations, previously destroyed by the process of hydrolysis of the hydronitracidium nitrate:



The destruction of the doubly charged ions necessarily leads to the accumulation of the singly charged cations $\text{NO}_2^+ \cdot \text{aq}$ (for example $\text{NO}_2^+ \cdot \text{H}_2\text{O} = \text{NO}(\text{OH})_2^+$), which are, as we have observed above, the basic nitrating agent for many chemical compounds. Here, obviously, may be found the answer to the well-known fact that 100% nitric acid nitrates cellulose, for example, more weakly than does the 95% acid. This cannot be explained from the point of view of the theory of nitration of Sapozhnikov.

Danilov, Matveev and Bukhalter (10) by comparing the degree of nitration with the process of swelling of cellulose in solutions of different concentrations have brought a high degree of clarity into the theory of nitration. Our explanation gives a new and additional degree of enlightenment with regard to this interesting and important problem.

Table 1
Contraction (in ml) during the reaction $\text{A} \cdot n\text{H}_2\text{O} + 0.1 \text{H}_2\text{O}$

Composition of the solution	Perchloric acid HClO_4 at 50°	Sulfuric acid H_2SO_4 at 20°	Selenic acid H_2SeO_4 at 20°	Acetic acid CH_3COOH at 20°	Methyl alcohol CH_3OH at 20°	Ethyl alcohol $\text{C}_2\text{H}_5\text{OH}$ at 20°	Propyl alcohol $\text{C}_3\text{H}_7\text{OH}$ at 15°	Isopropyl alcohol $\text{C}_3\text{H}_7\text{OH}$ at 15°	Glycerine $\text{C}_3\text{H}_5(\text{OH})_3$
A·0.0 H_2O	1.42	0.98	0.57	0.48	0.34	0.38	0.26	0.29	0.08
A·0.1 H_2O	1.25	0.83	0.55	0.36	0.30	0.31	0.20	0.27	0.08
A·0.2 H_2O	1.14	0.74	0.52	0.29	0.27	0.26	0.16	0.24	0.07
A·0.3 H_2O	1.07	0.67	0.50	0.24	0.22	0.23	0.14	0.21	0.07
A·0.4 H_2O	1.02	0.62	0.47	0.20	0.17	0.20	0.12	0.19	0.06
A·0.5 H_2O	0.97	0.57	0.44	0.18	0.16	0.18	0.12	0.18	0.06
A·0.6 H_2O	0.91	0.52	0.41	0.16	0.15	0.17	0.10	0.16	0.06
A·0.7 H_2O	0.86	0.47	0.36	0.14	0.14	0.15	0.10	0.15	0.06
A·0.8 H_2O	0.81	0.42	0.32	0.12	0.13	0.15	0.09	0.15	0.06
A·0.9 H_2O	0.76	0.37	0.29	0.11	0.11	0.14	0.09	0.14	0.06
A·1.0 H_2O	0.70	0.32	0.25	0.11	0.10	0.13	0.08	0.13	0.05
A·1.1 H_2O	0.54	0.28	0.24	0.10	0.09	0.12	0.08	0.13	0.05
A·1.2 H_2O	0.56	0.24	0.23	0.09	0.08	0.12	0.08	0.12	0.05
A·1.3 H_2O	—	0.22	0.22	0.09	0.07	0.11	0.07	0.11	0.04
A·1.4 H_2O	—	0.20	0.21	0.09	0.06	0.11	0.07	0.11	0.04

The addition of water to the 95% solution of nitric acid causes the hydrolysis of the remaining singly-charged nitronium cations. This process may take place in accordance with the following equation:



Thus, in strongly diluted aqueous solutions of nitric acid there is actually a complete absence of any nitrogen-containing cation — either doubly or singly charged — and because of this, the dilute solutions naturally cannot serve as nitrating solutions for many aromatic compounds. In such solutions

there is present, however, the nitrate ion (equation IX), which is a basic nitrating agent for aliphatic compounds [2].

Table 2

Contraction (in ml) during the reaction $\text{HNO}_3 \cdot n\text{H}_2\text{O} + 0.1\text{H}_2\text{O}$.

Composition of the solution $\text{HNO}_3 \cdot n\text{H}_2\text{O}$	Weight % HNO_3	At 5°/4°		At 20°/4°		At 30°/4°	
		sp. gr.	contraction	sp. gr.	contraction	sp. gr.	contraction
$\text{HNO}_3 \cdot 0.0\text{H}_2\text{O}$	100.000	1.5402	0.22	1.5129	0.19	1.4952	0.19
$\text{HNO}_3 \cdot 0.1\text{H}_2\text{O}$	97.221	1.5252	0.44	1.4982	0.43	1.4809	0.42
$\text{HNO}_3 \cdot 0.2\text{H}_2\text{O}$	94.592	1.5190	0.46	1.4924	0.45	1.4753	0.44
$\text{HNO}_3 \cdot 0.3\text{H}_2\text{O}$	92.101	1.5138	0.43	1.4875	0.42	1.4706	0.40
$\text{HNO}_3 \cdot 0.4\text{H}_2\text{O}$	89.738	1.5078	0.40	1.4819	0.39	1.4650	0.38
$\text{HNO}_3 \cdot 0.5\text{H}_2\text{O}$	87.493	1.5014	0.38	1.4759	0.37	1.4591	0.36
$\text{HNO}_3 \cdot 0.6\text{H}_2\text{O}$	85.358	1.4948	0.37	1.4697	0.35	1.4529	0.34
$\text{HNO}_3 \cdot 0.7\text{H}_2\text{O}$	83.325	1.4880	0.36	1.4633	0.34	1.4466	0.33
$\text{HNO}_3 \cdot 0.8\text{H}_2\text{O}$	81.386	1.4814	0.34	1.4568	0.33	1.4404	0.32
$\text{HNO}_3 \cdot 0.9\text{H}_2\text{O}$	79.536	1.4746	0.33	1.4505	0.32	1.4341	0.31
$\text{HNO}_3 \cdot 1.0\text{H}_2\text{O}$	77.767	1.4681	0.32	1.4441	0.30	1.4280	0.30
$\text{HNO}_3 \cdot 1.1\text{H}_2\text{O}$	76.076	1.4616	0.31	1.4378	0.30	1.4220	0.29
$\text{HNO}_3 \cdot 1.2\text{H}_2\text{O}$	74.457	1.4551	0.31	1.4316	0.29	1.4159	0.28
$\text{HNO}_3 \cdot 1.3\text{H}_2\text{O}$	72.905	1.4487	0.29	1.4254	0.27	1.4099	0.27
$\text{HNO}_3 \cdot 1.4\text{H}_2\text{O}$	71.416	1.4424	0.28	1.4194	0.27	1.4040	0.26

As is obvious from Tables 1 and 2, the two most practically important acids, sulfuric and nitric, behave differently toward water: 1 mole of sulfuric acid (98.08 g) upon mixing with 0.1 mole of water (1.80 g) gives a contraction of 0.98 ml, while 1 mole of nitric acid (63.02 g) upon mixing with the same amount, 0.1 mole of water (1.80 g), gives 1/5th of this contraction, 0.19 ml. It is therefore completely natural to suppose that during the mixing of very concentrated solutions of both acids, the hydrates of nitric acid give up their water, which goes to form hydrated molecules of sulfuric acid.

A very different picture is observed during the mixing of solutions of the composition $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{HNO}_3 \cdot \text{H}_2\text{O}$. Many investigators consider that under these conditions as well sulfuric acid plays the role of a dehydrating agent. However, volumetric calculations show otherwise: the contraction upon mixing 0.1 mole of water (1.80 g) at 20° is 0.32 ml, that is, practically the same as the contraction upon mixing 1 mole of $\text{HNO}_3 \cdot \text{H}_2\text{O}$ (63.02 g + 18.02 g = 81.03 g) with 0.1 mole of water (1.80 g), which is 0.31 ml. Thus, from the volumetric point of view, it is impossible to expect the transfer of water from one hydrate to the other.

The experiments of O. M. Voznesenskaya, carried out specially in our laboratory, have shown that the mixing of the solutions of the composition $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{HNO}_3 \cdot \text{H}_2\text{O}$, as well as the corresponding solutions of the compositions $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{HNO}_3 \cdot 2\text{H}_2\text{O}$, are in fact characterized by an almost complete absence of volumetric effect: the sum of the volumes of the initial liquids equals the volume of the mixture. This result shows, furthermore, that during the mixing of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ with $\text{HNO}_3 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ with $\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ there is no reaction between the sulfuric and nitric acids themselves. Both these last conclusions are without doubt of significant theoretical and practical interest.

SUMMARY

1. The present research was undertaken with the object of testing the correctness of the hypothesis that doubly charged nitronium ions $N(OH)_3^+$ are present in free nitric acid, and are decomposed during the dilution of the acid with water.

We must expect theoretically that the occurrence of such ions in nitric acid is responsible for the anomaly found in the contraction curve of solutions of nitric acid in comparison with contraction curves of solutions of other liquids.

2. Perchloric acid, sulfuric acid, selenic acid, acetic acid, methyland ethyl alcohol, propyl alcohol, isopropyl alcohol, and glycerine, in the process of mixing one after the other with the identical quantity of water, invariably reveal a contraction of the solution formed compared to the sum of volumes of the initial liquids.

The intensity of the contraction observed weakens upon further and further dilution of the solution. The contraction-composition curves for aqueous solutions of the liquids indicated have a similar appearance.

3. Nitric acid shows a sharply expressed anomaly. The first portion of water added to the acid gives a smaller contraction than the following portions. The maximum effect of the addition of water is shown by the 95% solution of nitric acid, which corresponds to a composition of $HNO_3 \cdot 0.2H_2O$.

The close connection between the volumetric behavior of nitric acid and its role as nitrating agent for different groups of chemical compounds has been considered.

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Received March 3, 1948

EQUILIBRIUM IN THE SYSTEM UREA-POTASSIUM BROMIDE-WATER

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The study of urea is being conducted nowadays in order to utilize it as a high quality nitrogen mineral fertilizer.

In the works of V.A.Sokolov [1] and V.P.Blidin [2], in our own work [3], and in others, investigations have been made of the solubility of urea in the presence of several mineral salts, which are themselves good fertilizers.

For a more thorough study of the physiological and biochemical processes of an organism, it is of interest to investigate the action of urea in the presence of various metal bromides which are utilized as medical preparations.

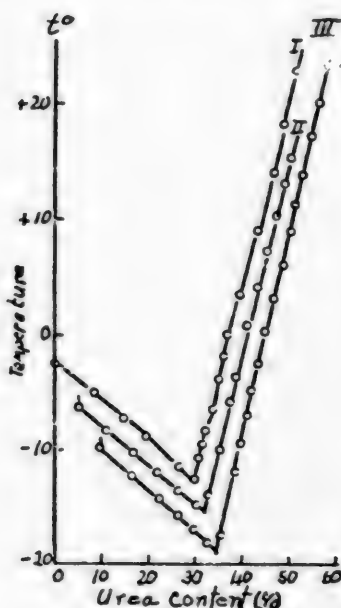


Fig. 1. Polytherms of cross-sections I, II, and III made in the urea direction.

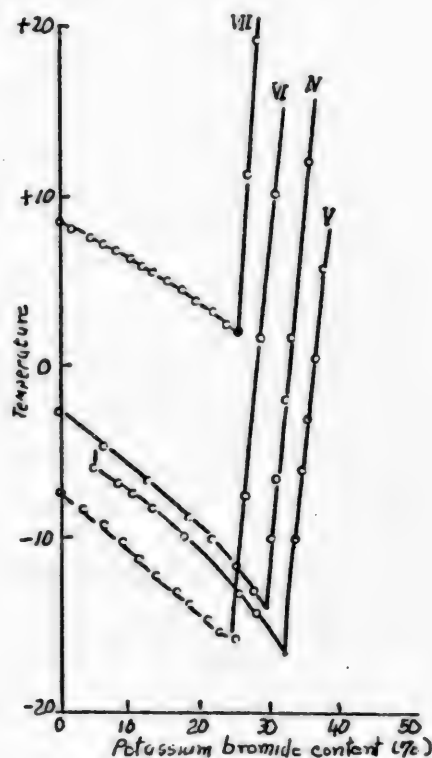


Fig. 2. Polytherms of cross-sections IV, V, VI, and VII, made in the potassium bromide direction.

The present work represents a polythermic investigation of the solubility of urea in the presence of potassium bromide. The work was carried out using a visual polythermic method at temperatures from +25° down to complete crystallization of the system. According to the data of R.K. Ozolin and M.I. Shakhparonov [4]

the eutectic point of the system urea-water corresponds to the composition: 32.9% urea, 67.1% water at a temperature of -11.1° . The urea branch has several discontinuities, which indicate the presence of polymorphic modifications of urea in the temperature range from 0 to 25° .

Table 1

90% H ₂ O + 10% KBr		80% H ₂ O + 20% KBr		72% H ₂ O + 28% KBr	
Weight % CO(NH ₂) ₂	t°	Weight % CO(NH ₂) ₂	t°	Weight % CO(NH ₂) ₂	t°
-	-2.5	-	-6.2	-	-9.8
8.46	-5.0	6.57	-8.2	7.06	-12.2
15.60	-7.1	12.33	-10.1	13.18	-14.3
19.78	-8.7	17.42	-11.8	16.84	-15.8
27.00	-11.4	21.96	-13.5	20.20	-17.0
30.14	-12.7	26.02	-14.8	23.30	-18.1
31.16	-10.8	28.50	-14.0	26.17	-17.5
32.33	-9.5	30.82	-10.0	28.83	-12.0
33.02	-8.4	32.99	-6.0	30.09	-9.5
34.38	-6.2	35.04	-3.6	31.30	-7.0
35.63	-3.8	36.96	+0.9	32.48	-4.8
36.90	-1.7	38.77	+4.5	33.61	-2.5
38.15	+0.2	40.48	+7.4	35.25	+0.5
40.04	+3.7	42.09	+10.3	36.80	+3.5
43.69	+9.1	43.52	+13.2	38.28	+6.3
46.34	+14.1	45.08	+15.3	39.70	+9.2
48.86	+18.7	-	-	41.05	+11.7
51.33	+23.0	-	-	42.34	+14.2
-	-	-	-	43.97	+17.4
-	-	-	-	45.52	+20.5
-	-	-	-	46.98	+23.4
-	-	-	-	48.37	+26.1

For the system potassium bromide - water, the numerical data for the solubility have been taken from the Handbook of phys.-chem. technical values of the Technical Encyclopedia [5].

Our data for the solubility of the system potassium bromide - water, introduced with the object of attaining greater precision, fully coincide. The eutectic point corresponds to the composition: 32.0% potassium bromide, 68.0% water, and a temperature of -11.8° .

According to the data of A.G. Bergman and N.A. Vlasov [6] this system has a homeomorphic transformation at a temperature of $+20^{\circ}$.

To obtain the diagram of the ternary system, we investigated seven cross-sections: three in the urea direction, and four in the potassium bromide.

Cross Section I: 10% KBr + 90% H₂O → CO(NH₂)₂
 Cross Section II: 20% KBr + 80% H₂O → CO(NH₂)₂
 Cross Section III: 28% KBr + 72% H₂O → CO(NH₂)₂
 Cross Section IV: 10% CO(NH₂)₂ + 90% H₂O → KBr
 Cross Section V: 20% CO(NH₂)₂ + 80% H₂O → KBr
 Cross Section VI: 35% CO(NH₂)₂ + 65% H₂O → KBr
 Cross Section VII: 45% CO(NH₂)₂ + 55% H₂O → KBr

Data for the cross-sections in the urea direction are given in Table 1.
 Data for the cross-sections in the potassium bromide direction are given in Table 2.

Table 2

90% H ₂ O+10% CO(NH ₂) ₂		80% H ₂ O+20% CO(NH ₂) ₂		65% H ₂ O+35% CO(NH ₂) ₂		55% H ₂ O+45% CO(NH ₂) ₂	
Weight % KBr	t°	Weight % KBr	t°	Weight % KBr	t°	Weight % KBr	t°
-	-2.5	-	-5.7	-	-7.1	-	+8.6
7.04	-4.5	1.98	-6.0	3.19	-8.0	2.17	+8.2
13.15	-6.4	3.88	-6.4	6.19	-9.0	4.24	+7.7
18.51	-8.4	5.71	-6.8	9.06	-10.0	6.25	+7.3
21.73	-9.8	7.48	-7.3	11.60	-11.2	8.10	+6.9
24.71	-11.2	9.17	-8.0	14.0	-12.1	9.97	+6.5
27.47	-13.0	10.81	-8.5	16.52	-12.9	11.72	+6.1
30.03	-10.0	12.39	-9.0	18.76	-13.7	13.41	+5.7
31.25	-6.5	13.92	-9.7	20.80	-14.5	15.07	+5.3
32.42	-2.0	18.18	-11.6	22.89	-15.0	17.40	+4.7
33.55	+1.5	20.80	-13.1	24.80	-15.6	19.6	+4.0
35.75	+12.0	23.26	-14.2	26.60	-7.2	21.65	+3.3
-	-	28.78	-10.0	28.36	+1.4	23.63	+2.6
-	-	29.79	-6.0	31.17	+9.8	25.59	+2.0
-	-	30.77	-3.0	-	-	27.40	+11.2
-	-	32.66	+0.5	-	-	28.56	+19
-	-	33.56	+5.5	-	-	-	-
-	-	-	-	-	-	-	-

On the basis of the cross-sectional data, the diagrams have been constructed. Diagrams of cross-sections in the urea direction are given in Fig. 1. Diagrams of cross-sections in the potassium bromide direction are shown in Fig. 2.

It is necessary to observe that the cross-sections in the urea direction hardly differ from the solubility curve of the binary system urea-water. This shows that the presence in the solution of potassium bromide has hardly any influence upon the solubility of urea.

In the temperature range from 25° to the temperature of solidification of urea, there are three modifications with transition points near 0 and 25°. Similar modifications are observed with urea in the presence of other salts, in this case, of potassium bromide. In addition to this, it can be seen that the

temperature of homeomorphic transformation of urea is lowered by the presence of potassium bromide.

The cross sections in the potassium bromide direction rise sharply upward. Potassium bromide in the range from 25° to the temperature of solidification has two homeomorphic modifications with transition points near 20°.

The temperature of homeomorphic transformation of potassium bromide is

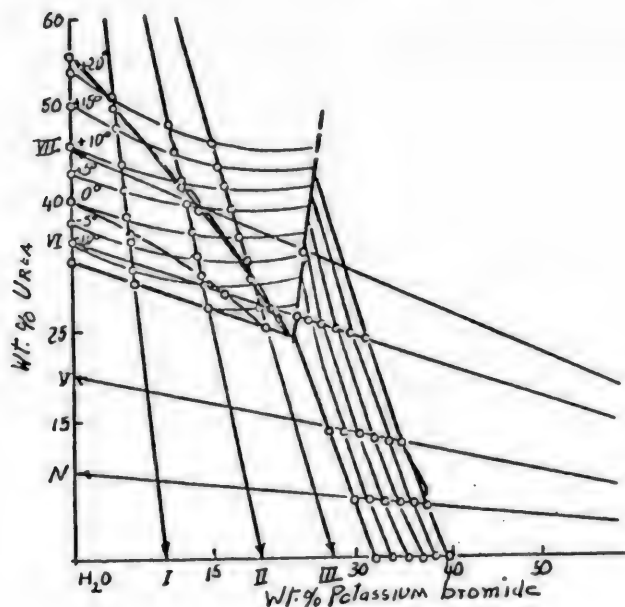


Fig. 3. Polytherms of the ternary system $\text{CO}(\text{NH}_2)_2 - \text{KBr} - \text{H}_2\text{O}$.

lowered by the presence of urea. We had earlier observed a similar type of lowering of the temperature of homeomorphic transformation by the presence of another salt in the system urea - potassium chloride - water. The data for the cross-sections are shown in the diagrams of the polytherms (Fig. 3), where the isotherms drawn through 5° have been obtained by interpolation.

As is evident from the diagrams and the cross-sections, the polytherms of the system are divided into six fields: ice, α and β potassium bromide, and α , β , and γ -urea.

The ternary eutectic point corresponds to the composition: urea 24.6%, potassium bromide 24.3%, water 51.1%, and temperature -20.8°.

SUMMARY

1. Solubility in the system urea - potassium bromide - water has been studied by a visual polythermic method.
2. The ternary eutectic point has been determined. It corresponds to a composition of 51.1% water, 24.6% urea, 24.3% potassium bromide, and a temperature of -20.8°.
3. No formation of new compounds has been observed in the system urea - potassium bromide - water.
4. Our earlier observation that the temperature of homeomorphic transformation of urea in the presence of other salts is lowered has been confirmed, and a similar phenomenon occurs with potassium bromide.

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Received February 17, 1948.

* Obvious typographical error.

PHYSICAL CHEMICAL STUDY OF IODINE SOLUTIONS

V.: THE THERMAL ANALYSIS AND ELECTRICAL CONDUCTIVITY OF THE SYSTEM PBr_5 -IODINE

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In a previous communication [1] we have presented the results of investigation of iodine solutions of phosphorus trihalides and phosphorus pentachloride.

These investigations have shown a significant difference between the behavior toward iodine of the phosphorus trihalides and PCl_5 : while the phosphorus trihalides do not form compounds with iodine, PCl_5 enters into a profound reaction with iodine, leading to the formation of the complex PCl_5I or $\text{PCl}_5\cdot\text{ICl}$, for which we may accept the structure $(\text{PCl}_4)(\text{ICl}_2)$. The electrolytic dissociation of this complex explains the high electrical conductivity of the system $\text{PCl}_5\text{-I}_2$, which attains a value of $4\cdot 10^{-2}$ reciprocal ohms.

In this connection it was of interest to investigate also the system $\text{PBr}_5 - \text{I}_2$, in order to compare the behavior of PBr_5 and PCl_5 in analogous systems.

The literature lacks information about the action of PBr_5 on iodine, except for the statement in the work of Gladstone in 1849,* to the effect that iodine reacts with PBr_5 according to the equation



This claim of Gladstone's is subject to doubt, inasmuch as the existence of IBr_3 has not yet been demonstrated.

EXPERIMENTAL

Iodine was purified as described in our previous paper. PBr_5 was prepared with a melting point of 103.7° .

The methods of investigation have also been described in our previous paper.

Thermal Analysis

The results of thermal analysis are shown in Table 1 and Fig. 1.

In the system $\text{PBr}_5 - \text{I}_2$, a eutectic was observed at 50 mol.% of PBr_5 and 13.5° .

The closer the system approached 50 mol % (either from the iodine or the PBr_5 side), the more difficult became the determination of equilibrium temperatures, in consequence of the high degree of supercooling, which reached 20° . In order to avoid this phenomenon, the first determination was always approximate, and repeated experiments were carried out with energetic stirring near the temperature of crystallization, thanks to which supercooling was reduced to 2 or 3° . We took into account only those experiments in which supercooling did not exceed this value.

After the eutectic, the temperature of crystallization increased up to 75 mol.% of PBr_5 , attaining at this concentration a maximum value of 110° ; near this, the second stationary temperature, corresponding to the eutectic (at 13.5°) disappeared, and instead there appeared a new second stationary temperature at 79° .

* We had no chance to consult Gladstone's original work.

It must be noted that the stationary temperatures observed with a PBr_5 content exceeding 75 mol. % were rather disconnected; but as the second stationary temperatures (around 79°) were observed during cooling of the melts containing

more than 75 mol. % of PBr_5 , they may be considered as being related to a second eutectic, and there is reason to suppose that the dystectic of the system $\text{PBr}_5 - \text{I}_2$ lies near 75 mol. % PBr_5 .

In this respect, the system $\text{PBr}_5 - \text{I}_2$ is analogous to the system $\text{PCl}_5 - \text{I}_2$ [1].

Thus the liquidus diagram of the system $\text{PBr}_5 - \text{I}_2$ indicates formation within it of a chemical compound. However, from the data obtained, just as during the investigation of the system $\text{PCl}_5 - \text{I}_2$, it is impossible to conclude that the maximum of the melting point curve (at 75 mol. % PBr_5) confirms the formation of a product which combines three moles of PBr_5 with 1 mole of iodine.

In order to decide the question of the nature of this chemical compound, it was supposed that in the system $\text{PBr}_5 - \text{I}_2$, such chemical reactions were possible as were in accord with the nature of the components of the system $\text{PCl}_5 - \text{I}_2$, in particular: the reduction of part of the PBr_5 to PBr_3 and the simultaneous formation of IBr , which with an excess of PBr_5 could give the complex $\text{PBr}_5 \cdot \text{IBr}$ or PBr_5I .

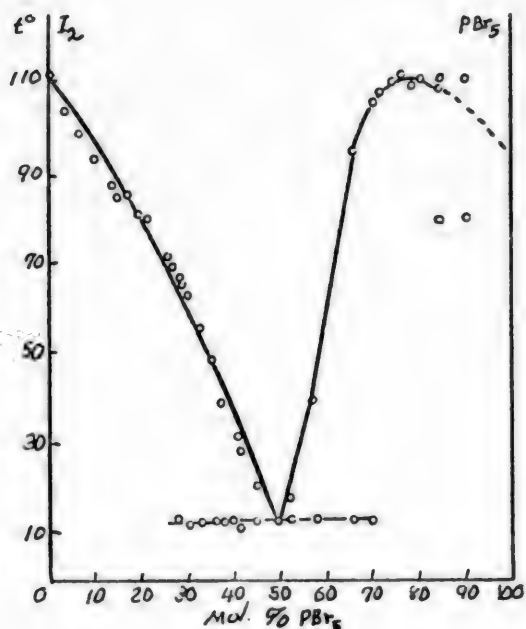
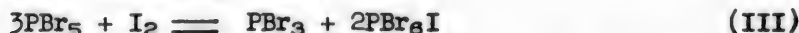
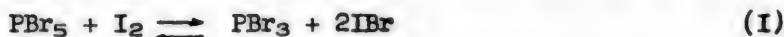


Fig. 1. Thermal analysis of the System $\text{PBr}_5 - \text{I}_2$



The formation of PCl_3 and PCl_5I in the system $\text{PCl}_5 - \text{I}_2$ can be shown directly, by distilling off the PCl_3 . In the present case a similar method of demonstration was impossible to carry out because of the high boiling point of PBr_3 (172°) and the thermal instability of the iodine bromide.

Therefore, the following experiments were carried out:

1. Starting with the fact that in accord with equation (I) PBr_5 and iodine, present in equimolecular ratios corresponding to the eutectic in the system, must react with each other to give for one mole PBr_3 2 moles IBr , we prepared a solution of PBr_3 with iodine bromide, containing 33 mole % PBr_3 , and determined the temperature of solidification of this solution. It was equal to 13.5° , the same as the temperature of solidification of the system $\text{PBr}_5 - \text{I}_2$ at 50 mole % PBr_5 .

This may serve as a demonstration of the fact that in the system $\text{PBr}_5 - \text{I}_2$, PBr_3 is actually formed, as well as IBr , as an intermediate product of the reaction.

Table 1

Thermal analysis of the system $\text{PbBr}_5 - \text{I}_2$

Concentration PbBr_5 (in mole %)	Stationary temperatures		Concentration PbBr_5 (in mole %)	Stationary temperatures	
	First	Second		First	Second
Iodine	113.2	—	41.2	28.2	11.5
4.5	103.8	—	45.0	20.2	13.0
7.1	99.0	—	49.3	—	13.5
10.6	93.0	—	50.4	—	13.5
14.2	87.0	—	53.1	17.5	13.5
14.9	85.0	—	57.9	39.0	13.0
20.1	81.5	—	65.7	94.0	13.5
22.1	79.5	—	69.1	105.0	13.5
26.2	71.0	—	72.4	107.0	—
26.3	70.9	—	74.7	109.5	—
28.1	66.5	13.5	75.8	110.1	—
28.6	65.5	13.0	78.2	108.2	—
30.4	63.0	12.5	80.2	110.0	—
33.2	56.0	13.0	84.3	108.0	79.0
36.3	48.0	13.0	89.0	110.5	—
37.6	38.5	13.0	90.0	109.4	79.2
40.5	32.0	12.5	100.0	103.7	—

2. A solution of PbBr_5 and iodine bromide in equivalent quantities was prepared. This solution solidified at 114.5° , forming needles of a dark red-brown color.

From this we may conclude that the maximum on the melting point curve, at 75 mole % PbBr_5 , equal to 110° , corresponds to the melting point of the complex with the composition $\text{PbBr}_5 \cdot \text{IBr}$.

These facts confirm the supposition made earlier to the effect that the final products of the interaction of PbBr_5 with iodine are PbBr_3 and $\text{PbBr}_5 \cdot \text{IBr}$, in accord with the overall equation (III).

Thus, the melting point diagram of the system $\text{PbBr}_5 - \text{I}_2$, as of the system $\text{PCl}_5 - \text{I}_2$, is complicated by the fact that it expresses a group of processes taking place within the system, among them the formation of the complex $\text{PbBr}_5 \cdot \text{IBr}$.

It is fully possible that this fact explains some of the discontinuity of the points on the melting point curve of the system $\text{PbBr}_5 - \text{I}_2$, especially within the range from 75 to 100 mole % PbBr_5 .

Electrical Conductivity of the System $\text{PbBr}_5 - \text{I}_2$

The electrical conductivity of this system was measured at 130° . The values of the specific electrical conductivity are shown in Table 2 and Fig. 2, the magnitudes of the molecular electrical conductivity in Table 3 and Figs. 3 and 4.

During the increase in the concentration of PbBr_5 , the electrical conductivity increases, at first slowly, then significantly faster, attaining a maximum value of $3.4 \cdot 10^{-2}$ reciprocal ohms in the range from 40-50 mole % PbBr_5 . In general, within the limits of concentration from 25 to 82 mole % PbBr_5 the electrical conductivity changes little or remains almost constant, varying from $1.3 \cdot 10^{-2}$ to $3.4 \cdot 10^{-2}$ reciprocal ohms. From 82 mole % PbBr_5 on, the electrical conductivity diminishes sharply, and can no longer be observed at 95.7 mole % PbBr_5 .

Table 2

Specific electrical conductivity of the system $\text{PBr}_5 - \text{I}_2$ at 130° .

Concentration PBr_5 (mole %)	$\times 10^{-5}$	Concentration PBr_5 (mole %)	$\times 10^{-5}$
Iodine	4.1	31.7	2800
5.4	7.6	41.3	3400
7.1	8.5	50.3	3400
8.8	13.0	60.0	3200
11.1	33.0	72.5	3200
12.8	51.0	81.4	3200
14.2	86.0	82.3	2300
20.4	76.0	83.5	1700
21.9	100.0	85.5	230
24.7	130.0	95.7	No electrical conductivity observed
28.3	220.0		

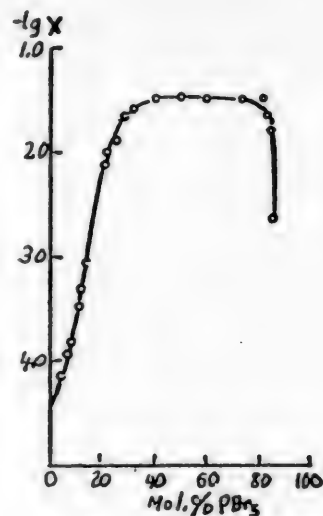


Fig. 2. Specific electrical conductivity of the system $\text{PBr}_5 - \text{I}_2$.

The electrical conductivity of the system $\text{PBr}_5 - \text{I}_2$ is very close to the value and the character of the isotherm for the electrical conductivity of the system $\text{PCl}_5 - \text{I}_2$, but in the latter system, the electrical conductivity increases much faster at initial concentrations of the phosphorus pentahalide than in the system $\text{PBr}_5 - \text{I}_2$.

These systems are distinguished also by the value of the temperature coefficient of electrical conductivity: in the system $\text{PBr}_5 - \text{I}_2$, it is negative.

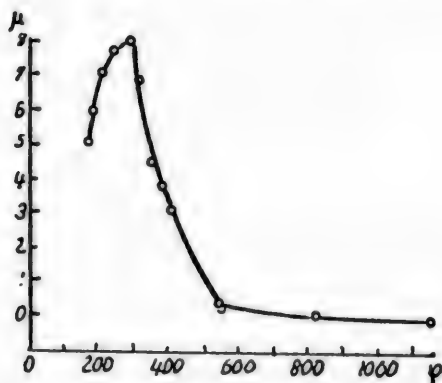


Fig. 3. Molecular electrical conductivity of the system $\text{PBr}_5 - \text{I}_2$, calculated on the basis of PBr_5 as electrolyte.

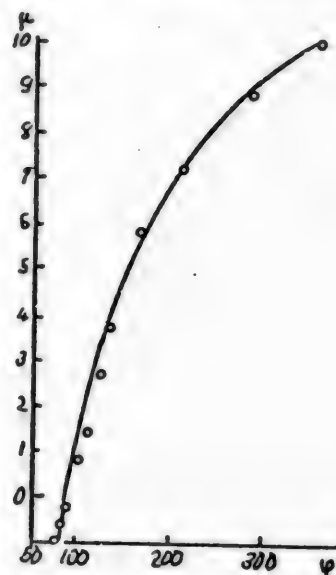


Fig. 4. Recalculated isotherm of the molecular electrical conductivity of the system $\text{PBr}_5 - \text{I}_2$.

Here, for example, are the data for 20.4 mole % PBr_5 :

Temperature	Specific electrical conductivity $\cdot 10^2$
100°	1.34
110	1.13
120	1.05
130	0.76

The molecular electrical conductivity of the system $\text{PBr}_5 - \text{I}_2$ has been calculated in two ways, with the electrolyte considered first as PBr_5 , and then as iodine (Table 3).

Table 3
Molecular electrical conductivity of the system $\text{PBr}_5 - \text{I}_2$

PBr_5 (mole %)	φ	μ	d	I_2 (mole %)	φ	μ
5.4	1193.1	0.09	3.78	94.6	73.7	0.006
8.8	821.4	0.11	3.72	91.2	79.4	0.01
12.8	548.4	0.28	3.64	87.2	80.9	0.04
14.2	547.1	0.47	3.61	85.8	89.9	0.08
20.4	402.4	3.06	3.52	79.6	103.5	0.78
21.9	380.9	3.81	3.50	78.1		
24.7	346.5	4.50	3.47	75.3	113.9	1.48
28.3	313.2	6.89	3.43	71.7	123.3	2.71
31.7	287.7	8.06	3.39	68.3	133.3	3.73
41.3	239.5	7.74	3.30	58.7	168.6	5.71
50.3	210.1	7.15	3.24	49.7	212.7	7.23
60.0	187.2	5.99	3.20	40.0	281.9	8.96
66.6	176.3	5.11	3.16	33.4	352.6	10.22

The specific gravity of the solutions was measured with a pycnometer at 130°, and is assigned the symbol d_{20}^{130} (Table 4 and Fig. 5).

The isotherm for the molecular electrical conductivity, calculated on the basis of PBr_5 as electrolyte (Fig. 3) has the appearance of a typical anomalous curve.

The recalculated curve for molecular electrical conductivity, (with iodine taken as the electrolyte) increases continuously upon dilution (Fig. 4).

These facts confirm the point that the high electrical conductivity of the system $\text{PBr}_5 - \text{I}_2$ must be ascribed to the electrolytic dissociation of the complex compound formed in this system.

The electrolyte in this case, the complex $\text{PBr}_5 \cdot \text{IBr}$ or $\text{PBr}_5 \text{I}$, has not yet been described in the literature.

In order to confirm the structure of this complex and the nature of the ions into which it dissociates, we prepared a solution of equimolar quantities of PBr_5 and IBr and then checked the electrolysis of its solutions in nitrobenzene.

The electrolysis was conducted in the vessel sketched in Figure 6. The electrodes

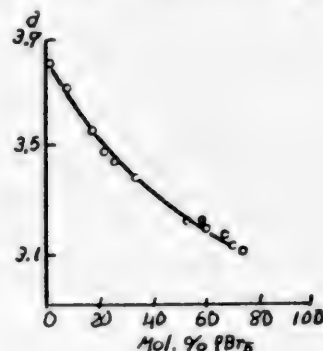


Fig. 5. Specific gravity of the system $\text{PBr}_5 - \text{I}_2$ at 130°.

* This vessel was more convenient than the one described in our previous article.

were of platinum. The solution for electrolysis contained 9.0% PBr_5I . The color of the solution was reddish-brown. The electrolysis was carried out at 240 volts. The initial strength of the current of 8 mA gradually decreased almost to zero. Length of electrolysis was 6 to 7 hours.

During the electrolysis, as during the analogous electrolysis of the nitrobenzene solution of PCl_5I , the color of the anode liquid gradually darkened, while the cathode liquid became noticeably lighter, approaching the color characteristic of nitrobenzene.

It was noted that bubbles of gas were given off at the cathode.

The analysis of the solutions was carried out as indicated in the previous communication, with the one difference that the iodine was determined by extracting with chloroform (after oxidation with a solution of NaNO_2) and then titrating with a solution of $\text{Na}_2\text{S}_2\text{O}_3$.

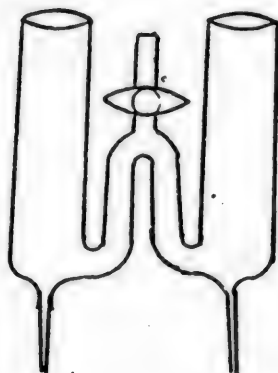


Fig. 6. Apparatus for the determination of the transport of ions.

The results obtained, given in Table 5, show that the iodine - in the form of a complex anion - is transported to the anode portion of the apparatus, which explains the decolorization of the cathode liquid.

The phosphorus was transported to the cathode section. This shows that the phosphorus enters into the composition of the cation, most probably, a complex one.

Table 4

Specific gravity of the system $\text{PBr}_5\text{-I}_2$ at 130°

Mole % PBr_5	d_{20}^{130}	Mole % PBr_5	d_{20}^{130}
Iodine	.91	51.70	3.23
1.93	3.84	57.80	3.20
8.51	3.73	59.20	3.19
17.30	3.57	64.90	3.18
22.20	3.47	66.22	3.16
26.90	3.44	71.05	3.11
32.80	3.37		

On the basis of analogy with the results of electrolysis of the nitrobenzene solutions of PCl_5I , we suppose that the structure of PBr_5I may be represented as $(\text{PBr}_4)^+(\text{IBr}_2)^-$.

Crystalline PBr_5 , according to the data of Powell and Clark (3) consists of tetrahedral ions $(\text{PBr}_4)^+$ and Br^- ions.

In this fashion, the formation of PBr_5I in the system $\text{PBr}_5 - \text{I}_2$, in accordance with the hypotheses expressed above, can explain the sequence of processes:

Table 5

Electrolysis of the system $\text{PBr}_5\text{I} - \text{C}_6\text{H}_5\text{NO}_2$

Concentration of PBr_5I in nitrobenzene (wt. %)	Material determined	Solution after electrolysis					
		Anode portion			cathode portion		
		Expected, g	found, g	Δ	expected, g	found, g	Δ
9.01	I	0.1280	0.2436	+0.1156	0.1265	0.0105	-0.1160
	P	0.0315	0.0226	-0.0089	0.0311	0.0406	+0.0095

1) the oxidation of iodine by the action of PBr_5 , with the resultant formation of PBr_3 and IBr ; 2) the combination of excess PBr_5 with the iodine bromide:



SUMMARY

1. Thermal analysis of the system $\text{PBr}_5 - \text{I}_2$ gives us reason to suppose that in this system a complex of the composition PBr_3I is formed, with a melting point of 114.5° .

This complex compound was also obtained by us upon melting together equimolar quantities of PBr_5 and IBr .

2. The results of electrolysis of the nitrobenzene solutions of PBr_3I - the transport of phosphorous to the cathode and of iodine to the anode - show that PBr_3I has a structure analogous to that of the compound PCl_3I , to wit: $[\text{PBr}_4]^+[\text{IBr}_2]^-$.

3. The high electrical conductivity of the system $\text{PBr}_5 - \text{I}_2$ makes clear the formation and the electrolytic dissociation of this complex.

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- [2] Gladston, Phil. Mag., 35, 345 (1849); Gmelins Handbuch, V. 8, 183 (1931).
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Received February 14, 1948.

*See CB translation p. 797 ff.

THE REACTION OF CALCIUM PHOSPHATES WITH CALCIUM HYDROXIDE AND CALCIUM CARBONATE

N. P. Malinovskaya

In the study of the reaction of phosphates and their utilization upon being introduced into the soil, the most essential questions brought to the fore by practice and awaiting decision, are the following:

- 1) In what forms do phosphates exist in soil solutions;
- 2) What sort of phosphate solid phases are the most stable under the various conditions that exist in the soil;
- 3) What is the solubility of the various little-soluble compounds of phosphorus under different conditions (the influence of temperature and pH) and what is the influence of the different factors on the mobility of phosphates (the introduction of lime, of potassium fertilizers, silica, and others);
- 4) What sort of phenomena take place on the interface of various little-soluble phosphates and solutions;
- 5) What sort of mechanism, and what laws, determine the absorption of phosphates by the soil?

The chief task of the present work was to study the reactions of the system: solid calcium carbonate - solid calcium phosphate - solution, that is, to study the influence of solid calcium carbonate upon the mobility of the phosphate at different values of pH. In addition, an attempt was made at an approach to the process of interaction of dibasic calcium phosphate with calcium hydroxide (with various quantities of the latter, that is, with different values of pH for the equilibrium solution), with the object of explaining the formation of one or another solid phase. As for the electrokinetic phenomena on the surface of the solid calcium carbonate in phosphate solution; we have already published data [1] on this question, and we shall not dwell upon them in the present work.

GENERAL

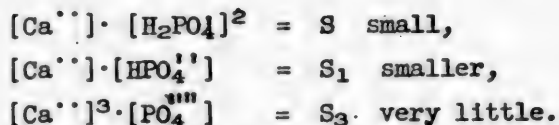
1. Ionic Forms of Phosphates in Aqueous Solutions Under Different Conditions

It is well known that phosphates exist in solution in the form of different ions, the relations between which are determined by the reaction of the medium (pH). Tables illustrating this relation have been given in the work already cited [1], and may be found there. With regard to the general equation for the condition of weak acids and its application to phosphoric acid in both dilute and more concentrated solutions, as well as to the dissociation constant of phosphoric acid, these questions are analyzed in fairly thorough detail in the work of B.P. Nikolsky, The Significance of pH in the Analysis of Natural Waters [2]. Here we consider it necessary only to recall that phosphoric acid in solution (and, consequently, also in soil solution) exists in the form of all three possible ions ($\text{H}_2\text{PO}_4'$, HPO_4'' , and PO_4''') and that one or another ion will prevail over the others depending upon the pH. Having taken into consideration the fact that the pH of soil in practice does not exceed 9, we may say with confidence that the

prevailing ions in soil solution are H_2PO_4^- and HPO_4^{2-} , and that if the PO_4^{3-} ions are present at all, they are in negligible quantity.

2. The Solid Forms of Phosphates under Different Conditions

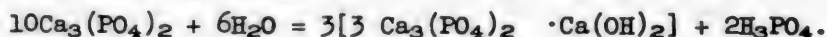
Corresponding to the phosphoric acid ions present, their different salts may be formed - in particular, the phosphates of calcium. It is possible to obtain one of the three calcium phosphates by precipitation from its solutions only in the case where the solubility product of its constituent ions is surpassed. A fairly long time ago, investigation showed that the solubility of calcium phosphates very strongly decreases as we pass from the mono- to the di- and tri-phosphates, and that consequently, their solubility constants decrease in the same order, that is:



Much work on the question of the solubility of calcium phosphates was carried out by Rindell [3] and a long series of other authors. We must observe that the results obtained by the different investigators differ fairly sharply from each other. The same Rindell explained these differences by the fact that equilibrium between the substances entering into the solution took place extremely slowly, but in addition, many authors did not make a complete analysis of the solution, limiting themselves only to the determination of Ca or P, at the same time as the author cited showed in his experiments that the amounts of Ca and P in solution were, as a result of hydrolysis, not equivalent. We must mention the more recent works of Domontovich and Zarubina [4], as well as the parallel work carried out by Holt, La Mer and Chown [5], which arrived at fairly similar results both during the study of the solubility of different calcium phosphates in water and in solutions of different electrolytes. Domontovich and Zarubina [4] give a graphic representation of the relation between the magnitudes of Ca, P_2O_5 , and pH, where it can be clearly seen how the concentration of phosphorus in the solution changes in a manner depending on the reaction of the last-named.

The indicated authors show, in their second work, that a more accurate quantitative study of the phenomena they have analyzed has become possible only in more recent years, thanks to the application of methods of measuring pH, and they carry out one of the first investigations in this field, in which they give various data on the influence of pH on the solubility of phosphates (this is according to the article by Atkins [6]).

More recently, interesting experiments on the hydrolysis of tertiary salts have been carried out by Lorah, Tartar, and Wood [7], who by boiling tricalcium phosphate with water and alkali for a long time obtained a fairly stable solid phase, analysis of which led them to the formula corresponding to the composition $3[\text{Ca}_3(\text{PO}_4)_2] \cdot \text{Ca}(\text{OH})_2$. During the boiling the solution developed a visibly acid reaction, and if the solution was removed or neutralized, then the reaction went to completion, and the composition of the precipitate did not change further. According to the opinion of the authors indicated, this hydrolysis could be expressed by the following equation:



In a survey of the literature, the cited authors point out that Warrington [8] had previously arrived at a similar formula, as best corresponding to his data for the analysis of the solid phase obtained by boiling tricalcium phosphate

with water, and had named the compounds of a similar type 'hydroxylated apatites'. The name 'hydroxyl-apatite' had been first suggested by Basset [9], who was unable to decide whether he was actually dealing with a material of an apatite-like structure, and not until 1932 and 1933 did Schleede, Schmidt and Kind [10], Tromel, [11], and several other authors [12] show roentgenographically that the characteristic apatite lattice was present in this compound. The hydroxyl-apatite was very stable toward the action of high temperature, and maintained its structure up to 1400°. In this respect, the compound was more stable than $\text{Ca}_3(\text{PO}_4)_2$, (Berzelius - phosphate [13]).

In connection with everything that has been stated above, the obtaining of any phosphate in the pure state (whether CaHPO_4 or $\text{Ca}_3(\text{PO}_4)_2$), both according to the majority of references in the literature and according to our own observations, is an exceedingly difficult task. The preparations obtained very often contain Ca and P in ratios that do not correspond to the formulas given. It is true that the literature does contain statements to the effect that by using certain methods under accurately controlled conditions, it is possible to obtain calcium phosphates with the theoretical ratios of CaO and P_2O_5 . We may refer, for example, to the work of Danneel and Frohlich [14]. For this reason, the question of the transformation of one solid phase of the phosphate into another appears all the more interesting to us.

It seemed to us possible to apply the phase rule to this transformation. That is, we assumed that during the conversion of one Ca salt into another (for example, the conversion of CaHPO_4 by means of the addition of $\text{Ca}(\text{OH})_2$ into a more basic salt, so that the transformation takes place without a change in the number of components) up to the point where two solid phases are present, the composition of the solution must not change (during the variation of p and t) as a result of the addition of $\text{Ca}(\text{OH})_2$, while the latter enters completely into the formation of the new compound. If the composition of the solution depends upon the pH, the most easily determined value, then consequently, the value of the pH must not change. When a complete transformation has taken place, and only a single, new, solid phase is present, there must be a sharp leap in the value of the pH, as we have acquired one more degree of freedom, permitting a change in the composition of the solution. The results obtained by us in these investigations did not completely correspond to these hypotheses, but we shall speak of these when considering our experimental data.

3. Solubility of Calcium Phosphates in the Presence of Solid CaCO_3

If we regard the solubility of calcium carbonate and calcium phosphates as a question in itself, then the solubility of calcium phosphates in the presence of calcium carbonate, both in our own and foreign literature, has received very little attention. There has been, however, a great deal of interest in the study of precisely this system in the field of agricultural chemistry. With regard to one of the latest and least elaborate works in this field, which appeared toward the time when we were finishing our experimental work, we must mention the work of Benne, Perkins, and King [15], in which the authors studied the solubility of phosphorus, adding to a given concentration of H_3PO_4 different amounts of Ca in the form of different compounds (CaO , CaCO_3 , soil saturated with Ca^{++}) and changed the pH by means of these compounds or by the addition of NaOH or HCl.

The basic conclusions from their work appear to be the confirmation of the fact that a marked precipitation of phosphoric acid takes place at a pH of 7.5 and higher, and that the action of soil saturated with Ca^{++} upon the solubility of P is similar to the action of CaCO_3 , with the exception that the solubility curve of the P in the first case (probably as a result of the absorptive

properties of soil) deviates somewhat from the solubility curve in the second case.

In the literature of agronomy - both at home and abroad - there are a great many works which deal with the influence of added lime on the mobility of phosphorus in the soil. We must note that here too there are great differences of opinion among the various authors. Most authors assert that when lime is added to the soil (considered as CaCO_3 , as well as CaO) and the amount of root-soluble phosphoric acid increases, this increase is due to the release of the phosphoric acid contained in the different soil compounds, as well as to the phosphate fertilizer added. For example, in the work of Yarusov, Pchelkin, and Dolgopolova [16], it is said that on the basis of their experiments with granular cultures, they have arrived at the conclusion that "the effectiveness of superphosphate was slightly increased by the addition of small quantities of lime, and that increased amounts of lime lowered the effectiveness of the superphosphate in proportion, due to precipitation." As for the effectiveness of phosphorites, the above-cited authors state that its diminution under the influence of added lime is even greater than with the above doses of lime. In the work of Yarusov and Tsentlin [17] they express the opinion that one of the causes of the increased availability to plants of the phosphoric acid of podzol soil upon addition of lime is the increase in mobility of phosphoric acid which had been held by the highly basic sesqui-oxides.

O. Engels [18] also arrives at the conclusion that the solubility of phosphoric acid upon the addition of lime to soils (both with CaCO_3 and CaO) may be increased to a greater or lesser extent, and that this increase of solubility depends both on the type of soil and on the degree of its acidity. O. Engels also considers as the cause of this phenomenon the transformation which lime produces in the soil, by extracting phosphoric acid from difficultly soluble compounds, both from other calcium compounds, and from phosphoric acid compounds which can easily be extracted from the roots of plants. It would be possible to cite a great number of works in this field, but we shall limit ourselves, and pass on to the presentation of our experimental work.

EXPERIMENTAL

Preparations

The work was conducted with the phosphate preparations of Merck and Kahlbaum, and in addition with carbonates and tertiary calcium phosphates prepared in our laboratory. The calcium carbonate was obtained by allowing fine jets of 0.1 N solution of pure calcium chloride to flow into an excess of 0.1 N solution of ammonium carbonate. When the precipitate had settled out, the 0.1 N solution of ammonium carbonate was decanted until the disappearance of the reaction for chlorine, then drawn on to a Buchner funnel through a close-packed filter, dried at 100° , and gently calcined. The calcium carbonate thus obtained, upon investigation by an electro-osmotic method, showed a positive charge, apparently to be explained by the fact that the concentration of Ca^{++} ions in solution was greater than the concentration of CO_3^{--} ions, thanks to the hydrolysis of the latter. The tertiary calcium phosphate was prepared by a method previously mentioned by Warrington [19], by pouring a dilute solution of $(\text{NH}_4)_2\text{PO}_4$ with ammonia present into a dilute solution of pure calcium chloride. The voluminous precipitate which settled out was washed by decantation with water (during the process, settling took place very slowly), filtered off, and dried. The phosphate obtained showed a positive charge, apparently, as in the case of the calcium carbonate, because of the hydrolysis of the PO_4^{--} ions. Analysis confirmed the fact that the amount of Ca in it was less than the amount which corresponded to the formula

$\text{Ca}_3(\text{PO}_4)_2$ (cf. general section). Analysis was also used to check on the calcium phosphates from the firms of Merck and Kahlbaum which were used during the work; according to the results, all the compositions differed from the one which was ascribed to them by the formula. In Table 1 are given the ratios in milli-moles of calcium to phosphate, both the theoretical, and those obtained as a result of analysis.

Table 1

Preparations	Theoretical Ca/P	Found Ca/P
Singly substituted calcium phosphate (Merck) $\text{Ca}(\text{H}_2\text{PO}_4)_2$	0.5	0.87
Singly substituted calcium phosphate (Kahlbaum) $\text{Ca}(\text{H}_2\text{PO}_4)_2$	0.5	0.84
Doubly substituted calcium phosphate (Merck for analysis) CaHPO_4	1.0	1.06
Doubly substituted calcium phosphate DAB ₃ (Kahlbaum) CaHPO_4	1.0	1.05
Triply substituted calcium phosphate (for analysis) $\text{Ca}_3(\text{PO}_4)_2$	1.5	1.49
Triply substituted calcium phosphate (own preparation)	1.5	1.34

The carrying out of the experiments, the results obtained, and their evaluation

The first question to interest us was the reaction of calcium phosphate with calcium hydroxide. In order to come to some conclusion about the conditions and the forms of phosphate in the solution and about the stability of the various solid phases, we conducted a series of experiments with the dibasic phosphates of calcium supplied by Kahlbaum (CaHPO_4). The experiments were carried out both in a series of small Erlenmeyer flasks, as well as in Shtomannovsky liter flasks. The first were conducted in the following manner: to the small Erlenmeyer flasks of Jena glass, with a capacity of 100 cc, blown out with CO_2 -free air, there were added batches of phosphate (0.2 g), then various (increasing) amounts of calcium hydroxide of known concentration were poured in, and the volume of liquid in all the flasks increased with CO_2 -free water to 75 cc. The flasks were shaken mechanically and the value of the pH in the solution determined with a glass electrode (directly in the flask). The shaking and the subsequent measurement of pH were repeated periodically in the course of many days.

The results obtained were so interesting that they led us not only to repeat the experiments, but also to carry them out with Merck preparations of CaHPO_4 . (In several series, the quantity of reagents were halved, that is 0.1 g of phosphate and a volume made up to 37.5 cc was used, with a corresponding quantity of $\text{Ca}(\text{OH})_2$. But the results of the first experiments were repeated with very good reproducibility: upon addition, there took place not alkalization, but an acidification of the solution up to a certain point, and only after the addition of a fairly large quantity of $\text{Ca}(\text{OH})_2$ was there observed a leap in the potential (the pH increased from 6.0, for example, up to 11.0). In time, the

curve was displaced downward, but the relative position of the points remained the same. All this may be seen in Fig. 1, on curves I and II, where the abscissa represents the cubic centimeters of $\text{Ca}(\text{OH})_2$ added, and the ordinate the pH of the corresponding system. Curve II represents the change of the process in time. The pH measurements were conducted for 25 days after those shown in Fig. 1.

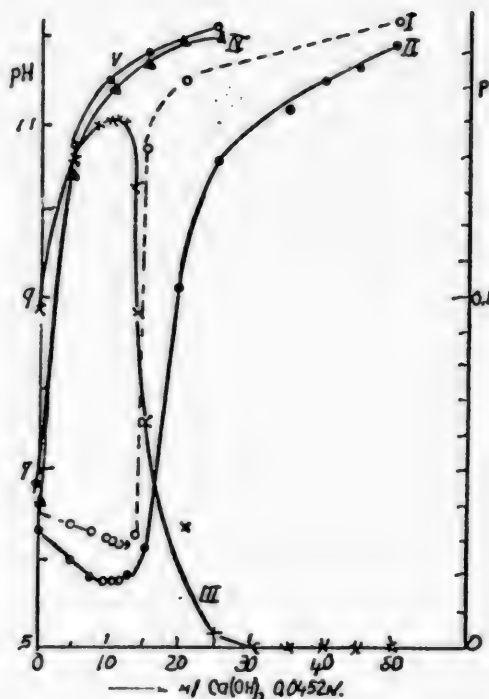


Fig. 1

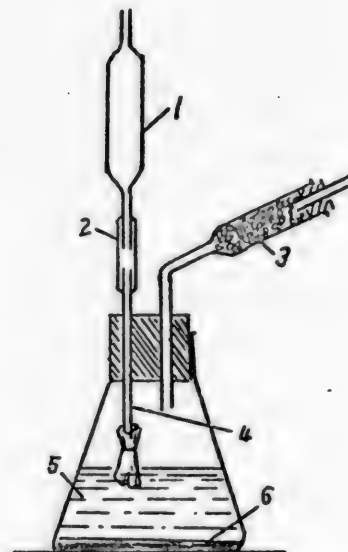


Fig. 2

1-pipette for sucking up the liquid; 2-rubber; 3-tube with soda lime; 4-glass tube with widened part at end, around which is wrapped the filter (blue cover) held by a rubber band; the end of the filter must be under the surface of the liquid; 5-settled solution; 6-precipitate.

In one of the series of experiments, not only was the pH measured, but the phosphate was determined colorimetrically and the alkalinity titrated with hydrochloric acid in the presence of phenolphthalein and methyl orange, while CO_2 -free air was blown through. The alkalinity thus determined was equivalent to the quantity of calcium. From the data obtained and from the quantities taken for the reaction of $\text{Ca}(\text{OH})_2$ with CaHPO_4 , the quantity of Ca and P in the precipitate was calculated, and their ratio at different moments of titration. We were chiefly interested in this ratio at the minimal values of pH. All these data (both those found and those calculated) are given in Table 2. They are in millimoles to the entire volume used, that is, to the 37.5 cc per 0.1 g portion of phosphate. The curve for the change in the quantity of phosphate follows (as was to be expected) a course the reverse of that of the pH curve (Fig. 1, curve III), that is, the concentration of phosphate in solution increases up to a definite limit corresponding to the minimum of the pH curve, and then, when the pH suddenly increases, a significant decrease of the amount of phosphate in the equilibrium solution occurs. As abscissas are plotted the cubic centimeters of $\text{Ca}(\text{OH})_2$ added at any given moment of titration and as ordinates the quantities

of phosphate present in millimoles in the corresponding equilibrium solution.

Samples of the equilibrium solution for the determination of phosphate colorimetrically and for the titration of alkalinity were taken by the method depicted in Fig. 2 in order to avoid turbidity from the precipitate and in order to remove the possibility of introducing CO_2 , which would be inevitable in the usual filtration. The liquid may be sucked up by this method either by mouth, or (taking the proper precautions) by means of a water-jet pump (Fig. 2).

From the data obtained in this series of experiments, several points for the carrying out of analogous experiments on a large scale were designated, in order to be able to investigate the equilibrium of the solution with greater accuracy and in more detail. For this purpose a quantity of phosphate and calcium hydroxide corresponding to 1 liter of solution was agitated in a liter Shtomannovski flask of Jena glass for six days, then the equilibrium solution was allowed to settle and a sample was siphoned off for analysis. In the equilibrium solution there were determined: pH, electrical conductivity, Ca^{++} , phosphorus, and in addition, the sign and magnitude of the charge on the precipitate. The experiments were carried out at pH 6.22 (pure phosphate), pH 5.87 with added $\text{Ca}(\text{OH})_2$, pH 5.61 with a greater quantity of added $\text{Ca}(\text{OH})_2$, and pH 6.59, with the addition of a still greater quantity of $\text{Ca}(\text{OH})_2$.

Table 2

No. of Expt.	$\text{Ca}(\text{OH})_2$ added to solution in millimoles	P in solution in millimoles	HCl consumed in reverse titration (in millimoles)	Total Ca (millimoles)	Total P (millimoles)	Ca in precipitate (millimoles)	P in precipitate (millimoles)	Ca:P in precipitate (millimoles)	pH of equilibrium solution
1	0	0.094	0.026	0.603	0.569	0.590	0.475	1.24	6.29
2	0.056	0.141	0.019	0.654	0.563	0.644	0.423	1.52	5.97
3	0.090	0.150	0.017	0.688	0.569	0.679	0.419	1.62	5.80
4	0.113	0.150	0.015	0.717	0.570	0.709	0.420	1.69	5.71
5	0.124	0.150	0.015	0.728	0.569	0.720	0.419	1.71	5.73
6	0.136	0.150	0.015	0.736	0.566	0.728	0.416	1.74	5.75
7	0.147	0.131	0.013	0.747	0.566	0.741	0.435	1.70	5.78
8	0.158	0.094	0.016	0.760	0.567	0.752	0.474	1.58	5.80
9	0.169	0.064	0.019	0.768	0.564	0.759	0.500	1.51	6.13

The data are given in Table 3. From the figures thus obtained it is still more obvious that the quantity of phosphorus in the solution varies greatly, in

Table 3

No. of expt.	CaHPO_4 added, g	$\text{Ca}(\text{OH})_2$ cc	0.0452 N (m-mole)	pH	Ca (mole-equiv./l)	P (mole-equiv./l)	$\text{H} \cdot 10^4$	ϵ (in mv)
1	2.659	0	0	6.22	3.104	2.486	2.1	+4.0
2	2.660	66.66	1.506	5.87	3.964	3.596	2.9	+3.8
3	2.661	133.35	3.014	5.61	4.120	3.513	2.9	+6.2
4	2.661	334.96 H_3PO_4 0.033 mole	7.57	6.59	0.452	0.363	0.44	+2.2
5	2.661	133.33	4.400	5.20	9.4	4.348	6.7	+5.6

a manner that depends on the pH, decreasing as the latter increases. A series of experiments, analogous to the experiments in the small flasks with the dibasic Ca phosphates, were carried out, both with Merck's triphosphates and with those we ourselves prepared. Here the phenomenon which took place with the dibasic phosphate (the lowering of pH upon the addition of $\text{Ca}(\text{OH})_2$, and consequently, also the increase in the amount of phosphorus in solution) was not observed. The curve rises sharply upward immediately upon the addition of calcium hydroxide (See Fig. 1, curves IV and V).

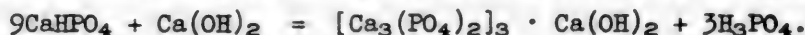
As a supplement, the same experiments on the action of calcium hydroxide upon phosphate were repeated also with preparations used in practice as phosphate



Fig. 3

fertilizers, in particular, with superphosphate, with phosphorite fertilizer, and with apatite. The phosphate fertilizer and the apatite appeared to be compounds of the tribasic type, and therefore, as was to be expected, under the action of calcium hydroxide, gave the same picture as the calcium triphosphate, that is, upon addition of $\text{Ca}(\text{OH})_2$ the pH of the system at once rose sharply (see Fig. 3). With superphosphate, which appears to be a primary compound, a different phenomenon took place, particularly at the beginning, when upon the addition of $\text{Ca}(\text{OH})_2$, the pH rose to a definite limit (to that value of the pH corresponding to the dibasic salt), after which the same results were obtained as with the Kahlbaum and Merck dibasic phosphates, *i.e.*, the pH fell to a definite point and the amount of phosphorus in the solution increased. Here this phenomenon was more clearly expressed than with the pure preparation of CaHPO_4 ; then there was a sharp discontinuity in the pH curve which was transformed into a smoothly rising curve. This can be seen in Fig. 3, where the coordinates are the same as the coordinates of Fig. 1. The lower curve represents a change in the process with

time. Measurements were carried out 12 days after the first (Fig. 3). The explanation of this interesting phenomenon, *i.e.*, the lowering of the pH and the increase in the quantity of phosphorus in the equilibrium solution upon the addition of calcium hydroxide to the dibasic calcium phosphate, must, in our opinion, be sought in the fact that during this reaction there is formed not the tertiary calcium phosphate, as might have been expected, but the compound with a higher Ca/P ratio, which is more stable under these conditions. This is the so-called hydroxyl-apatite, having the formula $3[\text{Ca}_3(\text{PO}_4)_2] \cdot \text{Ca}(\text{OH})_2$. During this reaction, phosphoric acid is set free, as a result of which the pH is lowered and the amount of phosphorus in the equilibrium solution is increased.



That this is the compound formed is shown by the closeness to the theoretical of the Ca/P ratio in the solid phase of our system at the lowest value of the pH. This ratio for hydroxyl-apatite is equal to 1.67, and in the solid phase of our system (as is evident from Table 2, experiment 4) is equal to 1.69.

The sharp discontinuity in the pH curve signifies that here the entire solid phase has been converted into the new compound, that is, into hydroxyl-apatite;

the further smooth rise of the curve indicates either that no other solid phase is formed, or that there is a compound of the adsorption type.

If we turn to the experiments of Lorah, Tartar, and Wood [7], we can say that the calcium hydroxide, strictly speaking, only hastens the process of formation of the hydroxyl-apatite, as the authors cited have shown that the phosphate is very slowly transformed into it by hydrolysis. As for the quantity of phosphate in solution, it is evident from Fig. 1 that its maximum value occurs at the minimum pH, after which it begins to fall fairly sharply and at a pH of 8.0 has already become practically negligible. If we again turn to the works which we have cited in the general section [18,19,20,21] and in which mention was made of the great effectiveness of lime on several phosphate fertilizers in the ground, it is possible that even if only partially, the explanation of this phenomenon must be sought in the process we have just considered. The increase in the effectiveness of phosphate fertilizers upon the addition of lime is observed likewise during the application of superphosphate, and does not take place (or there is even a reverse effect) in the use of such phosphate fertilizers as the phosphorites. This may have something to do also with the experiments determining the increase in the quantity of phosphates in soil solutions (increase in the mobility of phosphates in soils) upon the addition of lime to these soils.

Along with the experiments on the alkaline side (with the addition of $\text{Ca}(\text{OH})_2$), there was also carried out a series of experiments with the same CaHPO_4 , Kahlbaum, in acid solution, with the addition of corresponding quantities of phosphoric acid, H_3PO_4 , in order to clarify the behavior of phosphates at lower values of pH. It was shown that in the acid region there was no break in the values of pH, and the curve was gradually lowered, a fact which bespeaks the lack of formation of a new solid phase, or as we have already suggested, the formation of a compound of the adsorption type. The data are presented in Fig. 4. Along the axis of the abscissa are the cubic centimeters of phosphoric acid added, along the axis of ordinates the pH values of the equilibrium solutions.

A second question of interest to us was that of the solubility of calcium phosphate in the presence of calcium carbonate, inasmuch as the data on the solubilities of the calcium carbonate and phosphate, in the numerous researches devoted to them separately, are unsatisfactory, both with regard to their simultaneous presence in solution and with regard to the difference in reaction of the medium. We have already spoken of this in the general section of our paper. We carried out in sequence a series of experiments with pH values of 5.99, 6.10, 6.98, 7.77, 8.58, and 9.40. The experiments were performed as follows: 5 g CaCO_3 was mixed with CaHPO_4 in a liter Shtomannovski flask, which was then filled with distilled water up to the mark. The equilibrium solutions at low values of pH (5.99 and 6.10), obtained by passing CO_2 into them from a cylinder, shaking mechanically, were allowed to settle. Solutions at higher values of pH (6.98, 7.77, 8.58) were prepared by exhausting CO_2 from the previously prepared solution (filled to the mark with distilled water) using CO_2 -free air, with subsequent shaking and settling. The equilibrium solution with a pH value of 9.40 was obtained by boiling a previous solution (with pH 8.58), to which distilled water had been added up to the liter mark, while passing air through. In the settled,

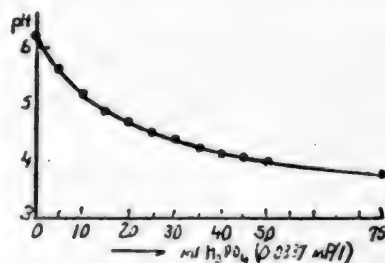


Fig. 4

transparent equilibrium solutions there were determined: pH, H, Ca, P, the electrometric titration curve. At the end, there were determined: A (the alkalinity), $\text{HPO}_4^{''}$, and $\text{H}_2\text{PO}_4'$. A, *i.e.*, the alkalinity of the equilibrium solution, was calculated as follows: before titration there was added to the solution an excess of hydrochloric acid, which was then titrated with calcium hydroxide. On the titration curve, the alkalinity was represented as the number of milli-equivalents of HCl, which corresponded to the titration at the moment when the pH became equal to the pH of the equilibrium solution. The ions $\text{H}_2\text{PO}_4'$ and $\text{HPO}_4^{''}$ could be calculated as in the following example: in the equilibrium solution (with pH 5.99) according to the data of the analysis, the amount of Ca was equal to 18.41 milli-equivs., and the alkalinity at the given pH was 16.65 milli-equivs.; consequently, the number of milli-equivs. of phosphoric acid ions was $18.41 - 16.65 = 1.76$, as there were no other ions in the given solution. During the analysis of the solution, we found 1.4 milli-moles of total P, but as at the given pH phosphoric acid could be considered practically all present in the form of singly- and doubly-charged ions, then:

$$[\text{H}_2\text{PO}_4'] + [\text{HPO}_4''] = 1.40 \text{ milli-moles,}$$

and in milli-equivalents:

$$2[\text{HPO}_4''] + [\text{H}_2\text{PO}_4'] = 1.76 \text{ milli-equiv.}$$

Indicating $[\text{HPO}_4'']$ by y and $[\text{H}_2\text{PO}_4']$ by x , we may solve the two equations:

$$x + y = 1.40$$

$$x + 2y = 1.76$$

$$y = [\text{HPO}_4''] = 0.36 \text{ milli-moles} = 0.72 \text{ milli-equivs.}$$

$$x = [\text{H}_2\text{PO}_4'] = 1.04 \text{ milli-moles} = 1.04 \text{ milli-equivs.}$$

The amount of phosphoric acid present in either form may be calculated also directly from the curve if we assume that $\text{H}_2\text{PO}_4'$ ions are present in the solution up to a pH value of 4.0, and that at higher values of the pH only $\text{HPO}_4^{''}$ ions are present. Then the difference between the total amount of Ca⁺⁺

and the amount present at pH 4.0 will determine $[\text{H}_2\text{PO}_4']$, and the difference between the latter and the alkalinity at the pH of the original solution $[\text{HPO}_4'']$.

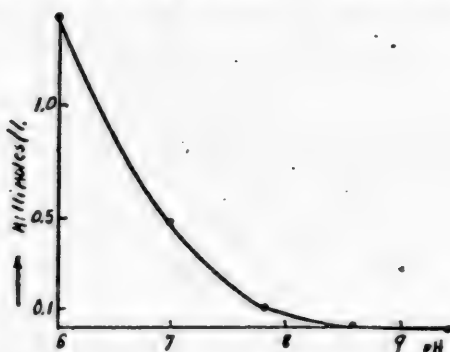


Fig. 5

From the data obtained, presented in Table 4 and Fig. 5, we may conclude that up to a pH of approximately 7.5-8.0, the presence of carbonate does not hinder the solution of the phosphates, but that at pH values above 8.0-8.5 phosphates are practically absent from the solution. This conclusion is confirmed by a study of the overcharging of CaCO_3 with regard to different phos-

phates, *i.e.*, that up to the limiting pH the phosphates are not in a position to change the charge of the Ca carbonate, but later on they also noticeably change their solubility [1]. In order to decrease this solubility, it is necessary to increase the pH of the system, as even in the presence of a great excess of CaCO_3 the pH of the equilibrium solution of the system $\text{CaHPO}_4 + \text{CaCO}_3$

is very low (about 7.0) and its charge is less than the charge of its components, as has been shown by our experiments on the overcharge of carbonate in relation to phosphates [1].

As in the soil we usually do not encounter a pH above 8 or 8.5, it follows that the addition of lime cannot have any influence upon the phosphates and throw the latter out of the soil solution. In table 4 are presented the figures for the analyses of six equilibrium solutions. In Fig. 5 is shown the change in the quantity of phosphorus in the equilibrium solutions in relation to pH. As abscissas are plotted the values of the pH of the solution, as ordinates the amount of phosphorus in it, expressed in milli-moles. In Fig. 6 are shown 6 separate curves. Each one corresponds to the titration of an equilibrium solution

Table 4

No. of Expt.	Treatment	pH of equilibrium solution by glass electrode	A according to titration curve (milli-equivs/li.)	Ca by analysis (milli-equivs/li.)	P		
					by analysis (milli-moles)	$[\text{HPO}_4^{ }] + [\text{H}_2\text{PO}_4^I]$ in milli-moles	$2[\text{HPO}_4^{ }] + [\text{H}_2\text{PO}_4^I]$ in milli-equivs.
1	5 g CaCO_3 in 1 liter H_2O saturated with CO_2 , shaken, and allowed to settle	6.10	19.56	19.56	—	—	—
2	5 g CaCO_3 + 5 g CaHPO_4 in 1 liter H_2O , sat. with CO_2 , shaken, and allowed to settle	5.99	16.65	18.41	1.40	1.40	1.73
3	From preceding system (after taking samples for analysis, diluting with water to 1 liter) air passed through without CO_2 , system shaken, and allowed to settle.	6.98	4.90	5.76	0.48	—	—
4	Preceding system (after taking samples for analysis, making up to 1 liter) continued passage of CO_2 -free air, shaken, and allowed to settle.	7.77	1.82	2.03	0.09	—	—
5	Preceding system (after taking samples for analysis, and making up to 1 liter), CO_2 -free air again passed through, shaken for a longer time, and allowed to settle.	8.58	0.58	0.72	0.02	—	—
6	Preceding system (after taking samples for analysis and diluting to 1 liter) boiled for 1 hr. with passage of CO_2 -free air, shaken, and allowed to settle.	9.40	0.32	0.42	0.002 colorimetric.	—	—

with a definite initial pH value, designated in Table 4. Along the axis of abscissas are plotted the amounts of HCl added, in milli-equivalents, determined in the solution at any given moment of titration, and along the axis of ordinates the pH of the solution at the same moment.

The amount of calcium in the solution, noted on the curve, is determined analytically (Table 4, Figs. 5 and 6).

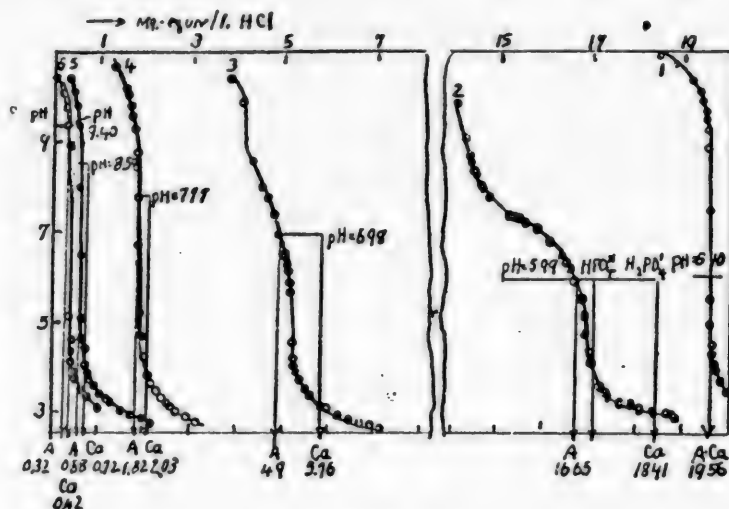


Fig. 6

In conclusion, we must say a few words about the methods used to analyze the equilibrium solutions. In all cases, these methods were conducted according to strict conditions. pH was determined by means of glass electrodes; it was in this manner that the electrometric titration curves were also obtained. The total quantity of phosphorus was determined by weight, by the method of double precipitation according to Voyu (precipitation with ammonium molybdate, solution in ammonia, and a second precipitation with magnesia mixture). The precipitation of the phosphorus was usually carried out after the separation of calcium, which was precipitated from acetic acid solution by ammonium oxalate (under these conditions, phosphoric acid remains in solution). If the phosphorus was present in minor quantity, it was determined colorimetrically by the method of Deniges, but in small porcelain crucibles instead of in colorimetric cylinders, a whole series being determined at once. Thus it was possible to compare the intensity of color in the solutions under investigation not only with the standards, but also with each other, which made the determinations significantly easier and more accurate. Calcium, after being precipitated in the manner already mentioned, with ammonium oxalate in acetic acid medium, was then determined by the method of Adams and Fisk, in the modification of I.I. Lavrov. The electrolytic potential was determined with an apparatus for the measurement of the value of the charge of powders, suggested in the physical chemistry laboratory LOVIUAA, the strength of the current measured with a milliammeter, and the electrical conductivity measured in the usual way, after Kohlrausch.

Tr. LOVIUAA, VASKHNIL, No. 43, 1936.

SUMMARY

1. Upon addition to the solid CaHPO_4 system of a solution of calcium hydroxide, there is first produced an acidification of the equilibrium solution and an increase in the quantity of phosphate in it up to a definite point, after which the pH suddenly rises, and the concentration of phosphate drops until it reaches a negligible value. This phenomenon is explained by the formation of the so-called hydroxyl-apatite $[\text{3Ca}_3(\text{PO}_4)_2]_3 \cdot \text{Ca}(\text{OH})_2$, which is more stable under these conditions. During this process, phosphoric acid is released, lowering the reaction of the equilibrium solution.

2. Upon the addition of $\text{Ca}(\text{OH})_2$ to the system superphosphate-solution, the same effects are produced as with CaHPO_4 , but only after the point where the initial compound $\text{Ca}(\text{H}_2\text{PO}_4)_2$ has been converted into the secondary CaHPO_4 .

3. In the reaction of $\text{Ca}(\text{OH})_2$ under these conditions with tricalcium phosphate, as well as with apatite and phosphorite fertilizer, the phenomenon just described is not observed — the pH immediately rises quickly.

4. The results of the experiments on the change of effectiveness of phosphate fertilizers in the ground with lime (cited in the general section and by many others) which shows an increase when superphosphate is applied, and no increase or even a decrease when phosphorites are applied, may be, at least in part, explained by the phenomenon described above.

5. The decrease in the solubility of phosphates in the presence of calcium carbonate, *i.e.*, the interaction of the latter with phosphates, takes place only when the solution is strongly alkaline. If the pH does not exceed 8.0, then in effect the CaCO_3 does not combine with the phosphates, and these are present in solution in reasonable quantity.

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Received April 15, 1948.

SPECTROPHOTOMETRIC INVESTIGATION OF COBALTOUS HALIDE COMPLEXES IN SOLUTIONS OF ETHYL ALCOHOL

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It is well known that solutions of the halide salts of bivalent cobalt in several nonaqueous solvents have a blue color analogous to that of their aqueous solutions in the presence of an excess of hydrogen halide acid.

Solutions of cobaltous chloride in ethyl alcohol, as can be seen from the work of Kiss [1] have increased absorption in the region from 600-700 m μ .

In this region of the spectrum absorption is strengthened upon the addition of hydrogen halide acid to aqueous solutions of cobaltous halides.

Several authors (Johnes and Uhler) who have studied the absorption spectrum of aqueous, alcoholic, and acetone solutions of cobaltous chloride, have expressed the opinion that the cause of the appearance of the blue color and the increase of absorption in the region of the spectrum from 600-700 m μ is dehydration of the cobalt ion.

However, the majority of authors explain the phenomenon in question by the appearance of complexes, most probably of compositions such as $\text{Co}(\text{Hal})_4^{--}$.

Dirking [2] who determined the molecular weight of cobaltous chloride and bromide in ethyl alcohol, found that these were greater than the theoretical (the latter corresponding to the formulas CoCl_2 and CoBr_2) and on this basis arrived at the conclusion that the complexes CoCl_4^{--} and CoBr_4^{--} were probably present in these solutions, although the values obtained for the molecular weights did not correspond to the values from the formulas of the indicated complexes.

The method for the determination of molecular weights which Dirking utilized could not give any other results, as it permits the determination of the molecular weights of compounds whose molecules are fairly stable and do not dissociate while the experiment is being conducted, something which cannot be said of complexes of the type $(\text{CoCl}_4)^{--}$ and $(\text{CoBr}_4)^{--}$.

The composition of this sort of complex, as Chugaev [3] has pointed out, does not permit the possibility of its being determined by this method.

We undertook to determine the composition of the complexes in alcoholic solutions of CoCl_2 , CoBr_2 , and CoI_2 by a method of continuous variation, utilized by us [4] during an analogous investigation of acetone solutions, which had been studied in order to determine the properties of solutions of different composition with regard to their optical density.

EXPERIMENTAL

The optical density was measured with a Beckman spectrophotometer at a temperature of $20^\circ \pm 1^\circ$.

As cobalt preparation, there was utilized $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (as the perchbr-ate is the least inclined to form complexes), prepared as described earlier [4].

Chemically pure ethyl alcohol was dehydrated up to 99.6% with anhydrous copper sulfate and subsequent distillation, and 99.9% alcohol was obtained by dehydration with metallic calcium, as described in the literature [5]

I. Cobaltous Chloride Complexes

In order to measure the optical density, mixtures of solutions of 99.6% alcohol were prepared with different contents of $\text{Co}(\text{ClO}_4)_2$ and LiCl in a constant volume of 5 ml and with a constant concentration of 0.1 m/l.

The LiCl preparation was obtained as previously described [4].

The technique of preparing the solutions can be seen from Table 1, in which are given the compositions of the solutions and the corresponding optical densities.

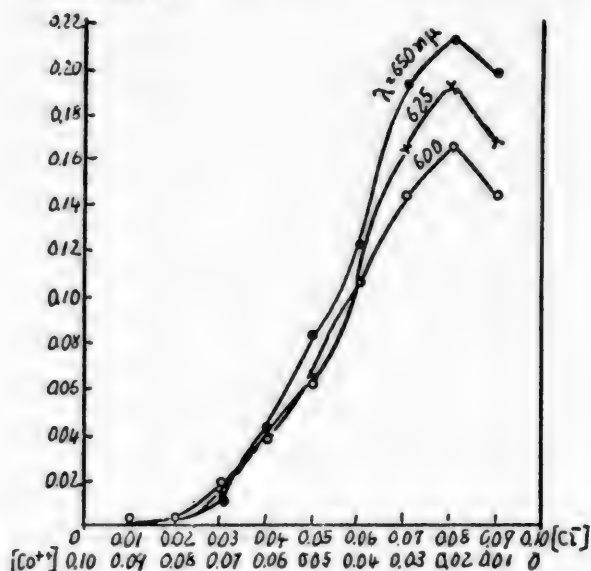


Fig. 1. Cobalt perchlorate + Lithium chloride in alcohol

The value of D was determined as the difference between the optical densities of the solutions $\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$ and $\text{Co}(\text{ClO}_4)_2$, using the same concentrations of cobalt perchlorate. (In table 1, the solutions of $\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$ are designated by Arabic numerals, those of $\text{Co}(\text{ClO}_4)_2$ by Roman).

As has been shown by Job [6] and Vosburg [7] a maximum or minimum on the curve plotting D against the composition gives the composition of the complex, which corresponds to the maximum or minimum absorption.

A graphic representation of the dependence of the value D upon the composition of the solutions is given in Fig. 1.

Table 1

Composition of solution					Optical density at λ (m μ) D at λ (in m μ)					
No.	0.1N sol. $\text{Co}(\text{ClO}_4)_2$ in ml	0.1 N sol. LiCl in ml.	Conc. in m/l $\text{Co}(\text{ClO}_4)_2$	LiCl	600	625	650	600	625	650
1	4.5	0.5	0.09	0.01	0.043	0.037	0.035			
I	4.5	—	0.09	—	0.048	0.040	0.038	0	0	—
2	4.0	1.0	0.08	0.02	0.045	0.037	0.035			
II	4.0	—	0.08	—	0.043	0.035	0.034	0.002	0.002	0.001
3	3.5	1.5	0.07	0.03	0.054	0.047	0.041			
III	3.5	—	0.07	—	0.038	0.033	0.030	0.016	0.014	0.011
4	3.0	2.0	0.06	0.04	0.068	0.065	0.068			
IV	3.0	—	0.06	—	0.031	0.027	0.026	0.037	0.038	0.042
5	2.5	2.5	0.05	0.05	0.088	0.089	0.105			
V	2.5	—	0.05	—	0.026	0.025	0.023	0.062	0.064	0.082
6	2.0	3.0	0.04	0.06	0.128	0.126	0.140			
VI	2.0	—	0.04	—	0.023	0.024	0.019	0.105	0.102	0.121
7	1.5	3.5	0.03	0.07	0.159	0.180	0.207			
VII	1.5	—	0.03	—	0.015	0.015	0.014	0.144	0.165	0.193
8	1.0	4.0	0.02	0.08	0.177	0.205	0.242			
VIII	1.0	—	0.02	—	0.012	0.012	0.010	0.165	0.193	0.232
9	0.5	4.5	0.01	0.09	0.150	0.175	0.205			
IX	0.5	—	0.01	—	0.006	0.008	0.006	0.144	0.167	0.199

The maximum of the curve leads to a composition of the solution of 0.02 m/l $\text{Co}(\text{ClO}_4)_2$ and 0.08 m/l LiCl , which corresponds to the composition of the complex $(\text{CoCl}_4)^{--}$.

The maximum absorption of the complex takes place in the region of the spectrum from 600 to 650 $\text{m}\mu$.

2. Cobaltous Bromide Complexes

Dirking's experiments on the determination of molecular weights showed that in ethyl alcohol there was an increase in molecular weight at a concentration of 0.2 m/l from 218.89 (theoretical molecular weight of CoBr_2) to 230.3 (theoretical molecular weight of CoBr_3 2.98.6; of CoBr_4^- 377.5). The observed increase of the molecular weight in comparison with the theoretical, as well as the anode transference of the blue alcohol solution, observed during the determination of transport numbers by Denham [2] forced us to assume the presence in the solution of a complex anion with the above-indicated composition.

We investigated a series of solutions of $\text{Co}(\text{ClO}_4)_2 + \text{LiBr}$ in 99.6% alcohol, prepared by the method of continuous variations.

The solutions of lithium bromide were prepared from twice recrystallized, chemically pure lithium bromide, dehydrated, after preliminary drying in a desiccator, and heated above 160° in a current of nitrogen.

Each solution was prepared in a volume of 5 ml with a total concentration of 0.1 M/l.

The composition of the solutions and the corresponding optical densities are given in Table 2.

Fig. 2 shows graphically how \bar{D} changes with the change in composition of the solutions

Table 2

No. of solution	Composition of solution				Optical Density at $\lambda(\text{m}\mu)$					\bar{D} at λ (in $\text{m}\mu$)				
	0.1 m. solution $\text{Co}(\text{ClO}_4)_2$ in ml.	0.1 M sol. LiBr in ml.	Concentration, m/l		600	625	650	675	700	600	625	650	675	700
			$\text{Co}(\text{ClO}_4)_2$	LiBr										
I	4.5	0.5	0.09	0.01	0.050	0.040	0.038	0.030	0.024					
I	4.5	-	0.09	-	0.048	0.040	0.032	0.030	0.023	0.002	0	0	0	0.001
2	4.0	1.0	0.08	0.02	0.054	0.042	0.040	0.032	0.023					
II	4.0	-	0.08	-	0.043	0.035	0.034	0.027	0.022	0.001	0.007	0.006	0.005	0.001
3	3.5	1.5	0.07	0.03	0.060	0.046	0.045	0.037	0.023					
III	3.5	-	0.07	-	0.038	0.033	0.030	0.026	0.018	0.022	0.013	0.015	0.011	0.005
4	3.0	2.0	0.06	0.04	0.060	0.060	0.056	0.054	0.031					
IV	3.0	-	0.06	-	0.031	0.027	0.026	0.019	0.011	0.029	0.033	0.030	0.035	0.020
5	2.5	2.5	0.05	0.05	0.075	0.079	0.075	0.075	0.040					
V	2.5	-	0.05	-	0.026	0.025	0.023	0.017	0.012	0.049	0.054	0.052	0.058	0.028
6	2.0	3.0	0.04	0.06	0.097	0.107	0.103	0.106	0.055					
VI	2.0	-	0.04	-	0.023	0.024	0.018	0.014	0.015	0.074	0.083	0.085	0.092	0.040
7	1.5	3.5	0.03	0.07	0.107	0.131	0.137	0.142	0.074					
VII	1.5	-	0.03	-	0.015	0.015	0.014	0.008	0.004	0.092	0.116	0.123	0.134	0.070
8	1.0	4.0	0.02	0.08	0.115	0.145	0.154	0.168	0.090					
VIII	1.0	-	0.02	-	0.012	0.012	0.010	0.006	0.004	0.108	0.133	0.144	0.162	0.086
9	0.5	4.5	0.01	0.09	0.085	0.113	0.122	0.135	0.077	0.079	0.105	0.116	0.131	0.077
IX	0.5	-	0.01	-	0.006	0.008	0.006	0.004						

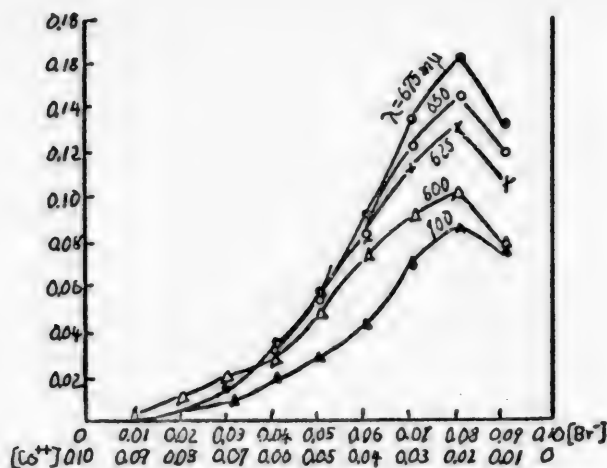


Fig. 2. Cobalt perchlorate plus lithium bromide in alcohol

The curve for \bar{D} against composition shows a maximum for the solution whose concentration is 0.02 in $\text{Co}(\text{ClO}_4)_2$ and 0.08 in LiBr , corresponding to the composition of the complex CoBr_4^{2-} .

The maximum absorption was found in the region of the spectrum from 600-700 $\text{m}\mu$.

3. Cobaltous Iodide Complexes

The existence of these complexes has been assumed chiefly on the basis of the work of Brode and Morton [8], who measured the absorption curve of CoI_2 solutions in concentrated hydriodic acid; it was entirely similar to the absorption curve of CoBr_2 in concentrated hydrobromic acid and of CoCl_2 in concentrated hydrochloric acid, with the exception

that it was displaced in the direction of lower frequency and extended into the infrared section of the spectrum. The composition of the cobaltous iodide complexes was determined in a manner analogous to that for CoCl_4^{2-} and CoBr_4^{2-} .

During investigation of the alcohol solutions of $\text{Co}(\text{ClO}_4)_2 + \text{LiI}$, we noted that the value of \bar{D} decreased (in solutions of uniform composition) from $\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$ to $\text{Co}(\text{ClO}_4)_2 + \text{LiI}$, i.e., the maximum value of \bar{D} was that for the solutions $\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$ and the minimum value for $\text{Co}(\text{ClO}_4)_2 + \text{LiI}$.

Table 3

No. of solution	Composition of solutions				Optical Density at λ (in $\text{m}\mu$)		\bar{D} at λ (in $\text{m}\mu$)	
	0.2 m solution CoCl_2 in ml	0.2 m solution LiI in ml	Conc. in ml.					
			CoCl_2	LiI	600	700	675	700
1	4.5	0.5	0.18	0.02	0.046	0.033	0	0.001
I	4.5	—	0.18	—	0.047	0.032		
2	4.0	1.0	0.16	0.04	0.042	0.028	0.002	0.002
II	4.0	—	0.16	—				
3	3.5	1.5	0.14	0.06	0.037	0.025	0.007	0.005
III	3.5	—	0.14	—	0.035	0.023		
4	3.0	2.0	0.12	0.08	0.036	0.024	0.009	0.007
IV	3.0	—	0.12	—	0.029	0.019		
5	2.5	2.5	0.10	0.10	0.034	0.025	0.010	0.008
V	2.5	—	0.10	—	0.025	0.018		
6	2.0	3.0	0.08	0.12	0.030	0.022	0.011	0.009
VI	2.0	—	0.08	—	0.020	0.014		
7	1.5	3.5	0.06	0.14	0.025	0.019	0.013	0.012
VII	1.5	—	0.06	—	0.014	0.010		
8	1.0	4.0	0.04	0.16	0.025	0.020	0.015	0.018
VIII	1.0	—	0.04	—	0.012	0.008		
9	0.5	4.5	0.02	0.18	0.015	0.011	0.008	0.005
IX	0.5	—	0.02	—	0.007	0.006		

It was impossible to determine the composition of the complexes in solutions of 99.6% alcohol at concentrations of 0.1 M/l because of the small value of \bar{D} , which lay within the limits of error of the measurements.

Because of this, solutions of $\text{Co}(\text{ClO}_4)_2$ and LiI were prepared in 99.9% alcohol.

The total concentration in each solution was increased to 0.2 M/l.

The alcohol solutions of lithium iodide were prepared from anhydrous chemically pure preparations of LiI , whose composition was checked analytically.

The composition of the solutions and the corresponding optical densities are given in Table 3.

Fig. 3 shows the curve of \bar{D} against composition with a maximum at the point corresponding to a concentration of 0.04 M/l $\text{Co}(\text{ClO}_4)_2$ and 0.16 M/l LiI , which represents a complex of the composition CoI_4^- .

Thus, the investigation of the solutions $\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$; $\text{Co}(\text{ClO}_4)_2 + \text{LiBr}$, $\text{Co}(\text{ClO}_4)_2 + \text{LiI}$ in ethyl alcohol by the method of continuous variation, and the measurements of the optical density of the solutions, have resulted in showing the presence of the complexes CoCl_4^- , CoBr_4^- , and CoI_4^- , whose existence had been assumed on the basis of the investigations of other physical chemical properties of the solutions in question.

The difficulty of investigation of the cobaltous iodide complex in comparison with the cobaltous chloride compound is apparently related to the decrease in stability of the complex in alcohol solutions as we go from (CoCl_4^-) to (CoI_4^-) .

SUMMARY

1. The ethyl alcohol solutions of the systems $\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$, $\text{Co}(\text{ClO}_4)_2 + \text{LiBr}$, and $\text{Co}(\text{ClO}_4)_2 + \text{LiI}$, have been investigated by the method of continuous variations, and by the measurement of their optical densities.
2. The presence of the complexes CoCl_4^- , CoBr_4^- , and CoI_4^- has been shown.
3. The stability of the complexes decreases from cobaltous chloride to cobaltous iodide.

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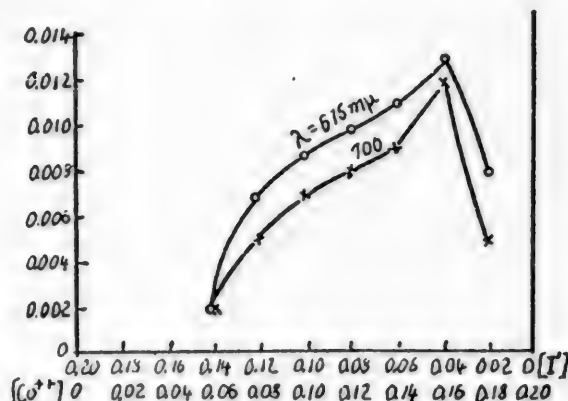


Fig. 3. Cobalt perchlorate + lithium iodide in alcohol

ALLYL REARRANGEMENTS

XI. ACTION OF ISOMERIC METHOXY-CHLOROPENTENES

ON Na-ALKYL ACETOACETIC ESTERS

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In one of our previous communications [1], we described the reaction between isomeric methoxychlorpentenes and metallic derivatives of malonic and acetoacetic esters. It was shown that the reaction of primary methoxychlorpentene, 1-methoxy-5-chlorpentene-3, with Na and Mg malonic esters proceeded normally, but with secondary methoxychlorpentene, 1-methoxy-3-chlorpentene-4, there was a complete allyl rearrangement. With regard to the analogous reactions with sodium acetoacetic ester, it was shown that with the primary methoxychlorpentene the reaction proceeded normally, according to the bimolecular type, and led to the formation of a mixture of mono- and disubstituted derivatives of acetoacetic ester, but with the secondary methoxychlorpentene there was formed a complicated mixture of products, boiling over a wide range of temperature.

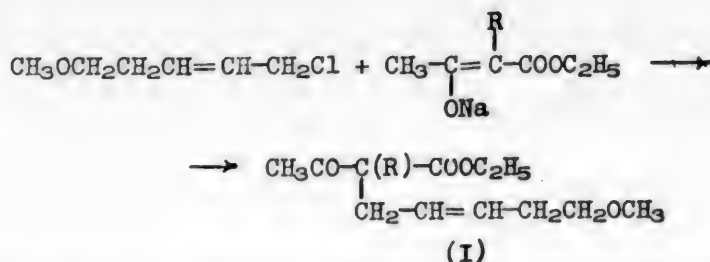
The experiments undertaken for the purpose of studying these reactions with Mg acetoacetic ester also did not lead to satisfactory results, as the yields of products of the reaction, even for the more reactive primary methoxychlorpentene, were very insignificant.

Under such circumstances, we were impelled to plan a series of experiments on the study of the reaction between isomeric methoxychlorpentenes and Na derivatives of various alkylacetoacetic esters. In the present communication there is a description of the results obtained by studying the reaction with Na derivatives of methyl, ethyl, propyl, and butyl acetoacetic esters.

The reactions were carried out in the usual manner [2] in a solution of absolute alcohol. As a result of the reactions between primary methoxychlorpentene and the sodium derivatives of the indicated alkylacetoacetic esters, the corresponding disubstituted acetoacetic esters were obtained, in yields of from 65 to 80%. In addition to the esters, in each of the reactions indicated, there was observed the formation of a small quantity of product boiling from 30 to 40° below the disubstituted acetoacetic ester. It was noted that the amount of this product under different conditions of experiment could vary between fairly wide limits.

The structure of the disubstituted acetoacetic esters obtained was confirmed by elementary analysis, the determination of the molecular refractivity, titration with bromine, and oxidation by potassium permanganate. As a result of the oxidation of n-butyl-n-methoxypentenylacetoacetic ester, methoxypropionic acid was obtained with a yield of 49%. The constants of the esters obtained are given in Table 1.

On the basis of the results obtained, it was possible to arrive at the conclusion that the formation of disubstituted esters during the reaction of primary methoxychlorpentene with sodium alkylacetoacetic esters proceeded normally, according to the equation:

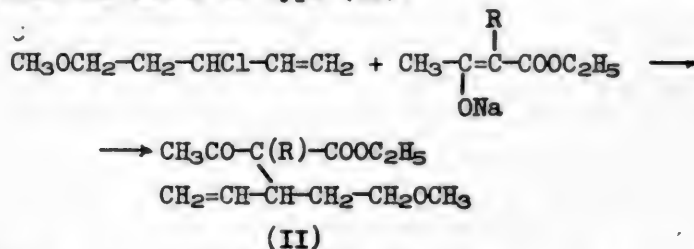


The reactions between secondary methoxychlorpentene and sodium alkylacetoacetic esters proceeded at a significantly lower speed than the reactions of the primary compound, and led to the formation, basically, of products identical with regard to the constants already cited with the low-boiling products obtained in small quantity during the analogous reactions with the primary methoxychlorpentene. There could be isolated, in insignificant quantities, and not in all cases, the disubstituted acetoacetic esters, also identical with those obtained from the primary methoxychlorpentene.

Table 1

Product No.	Formula	Boiling point	n_D^{20}	d_4^{20}	MR _D	
					calc.	Found
1	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CO}-\text{C}-\text{COOC}_2\text{H}_5 \\ \\ \text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2\text{OCH}_3 \end{array} $	148° at 8 mm	1.4500	0.9964	65.07	65.27
2.	$ \begin{array}{c} \text{CH}_3\text{CO}-\text{C}(\text{C}_2\text{H}_5)-\text{COOC}_2\text{H}_5 \\ \\ \text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2\text{OCH}_3 \end{array} $	169° at 18 mm	1.4515	0.9916	69.69	69.58
3	$ \begin{array}{c} \text{CH}_3\text{CO}-\text{C}(\text{C}_3\text{H}_7)\text{COOC}_2\text{H}_5 \\ \\ \text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2\text{OCH}_3 \end{array} $	147° at 5 mm	1.4530	0.9783	74.31	74.58
4	$ \begin{array}{c} \text{CH}_3\text{CO}-\text{C}(\text{C}_4\text{H}_9)\text{COOC}_2\text{H}_5 \\ \\ \text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2\text{OCH}_3 \end{array} $	176° at 14 mm	1.4525	0.9678	78.93	79.21

Thus, in the reactions with sodium alkylacetoacetic esters, there were formed from the primary and secondary methoxychlorpentenes mixtures of the same products, but in different proportions. It could be assumed that the formation of the low-boiling products in the reactions of the secondary methoxychlorpentene proceeded exactly as with the primary isomer, with the formation of disubstituted derivatives of acetoacetic ester of type (II):



A study of the properties of the products, however, showed the untenability of this assumption. It was found that the values obtained for the molecular

refraction of the products were almost three units higher than the theoretical values calculated from formula (II).

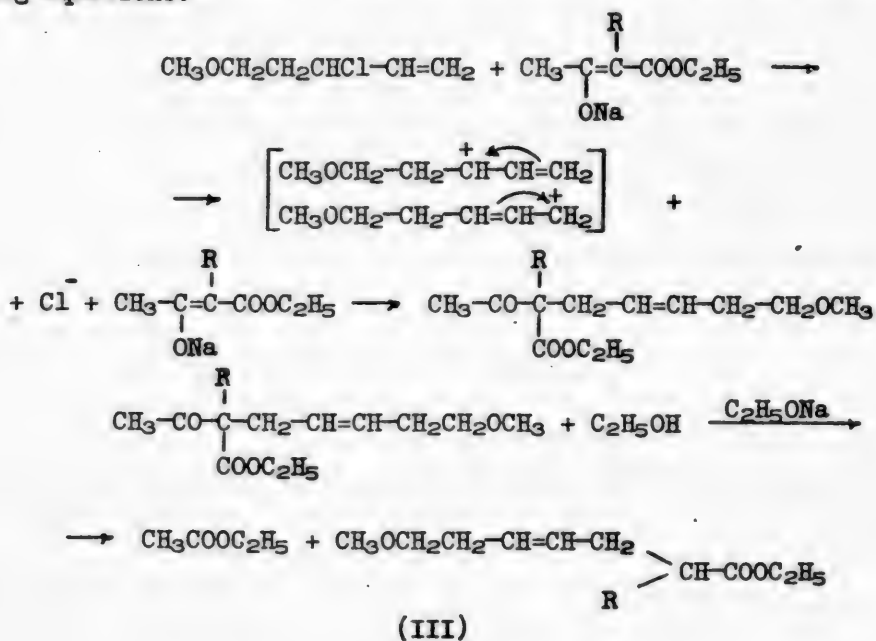
Elementary analysis of the products gave on an average 1.5% more carbon and 1.0% more hydrogen than corresponded to formula (II). A calculation of the empirical formulas of the products, according to the data of analysis, showed that they all differed from the empirical formula of (II) by one and the same group, C_2H_2O .

On the basis of these results, we arrived at the conclusion that the formation of the products indicated might be explained by the fact that a secondary reaction had taken place between the first formed disubstituted acetoacetic esters and alcohol in the presence of sodium alcoholate or sodium alkylacetoacetic ester. Under the action of the sodium alcoholate and alcohol there took place an ester cleavage of the disubstituted acetoacetic esters, with the formation of ethyl acetate and the ethyl ester of the disubstituted acetic acid.

Actually, it was shown that the alcohol distilled from the reaction mixture always had the characteristic odor of ethyl acetate. Titration of the products with bromine according to the MacIlliny method showed the presence of double bonds; the molecular refraction observed corresponded well with that calculated theoretically according to the formulas of the esters corresponding to the disubstituted derivatives of acetic acid (III).

As the same products were formed from primary and secondary methoxychlorpentenes, it was concluded that the reactions between secondary methoxychlorpentenes and sodium alkylacetoacetic esters proceeded according to the monomolecular type, with a complete allyl rearrangement. This was conclusively demonstrated by the oxidation of the product obtained in the reaction between secondary methoxychlorpetene and sodium butylacetoacetic ester with potassium permanganate; there were obtained methoxypropionic acid in 48% yield and the ethyl ester of butylsuccinic acid in 63% yield.

Thus, the course of the reaction between secondary methoxychlorpentene and the sodium derivatives of alkylacetoacetic esters may be expressed by the following equations:



It is obvious that the analogous cleavage of disubstituted acetoacetic esters takes place also in the reactions with primary methoxychlorpentene, exactly as already indicated above, but to a lesser extent; the esters of the disubstituted acetic acid are also formed, but in significantly smaller quantities. The constants obtained for the esters of the disubstituted acid are given in Table 2.

Table 2

No. of product	Formula	Boiling point	n_D^{20}	d_4^{20}	MR _D	
					calc.	Found
1	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}-\underset{\text{CH}_3}{\text{CH}_2}-\text{CH}-\text{COOC}_2\text{H}_5$	118.5° at 16 mm	1.4370	0.9342	55.83	56.10
2	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}-\underset{\text{CH}_3-\text{CH}_2}{\text{CH}_2}-\text{CH}-\text{COOC}_2\text{H}_5$	128-129° at 17 mm	1.4380	0.9287	60.45	60.49
3	$\text{CH}_3\text{OCH}_2\text{CH}_2-\text{CH}=\text{CH}-\underset{\text{CH}_3-\text{CH}_2-\text{CH}_2}{\text{CH}_2}-\text{CH}-\text{COOC}_2\text{H}_5$	120° at 5.5 mm	1.4400	0.9218	65.06	65.16
4	$\text{CH}_3\text{OCH}_2\text{CH}_2-\text{CH}=\text{CH}-\underset{\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2}{\text{CH}_2}-\text{CH}-\text{COOC}_2\text{H}_5$	145-146° at 12 mm	1.4415	0.9180	69.68	69.75

The difference between the proportions of products formed in the reactions with the primary and secondary methoxychlorpentenes can be explained, in our opinion, by the difference in their reactivities. The formation of disubstituted acetoacetic esters in the case of primary methoxychlorpentene, thanks to its greater reactivity, proceeds at a significantly greater speed than the reaction which results in the cleavage of the ester formed; the corresponding products of reaction tend almost entirely to be disubstituted esters of acetoacetic acid. In the case of secondary methoxychlorpentene, thanks to its considerably lower reactivity, the formation of the disubstituted derivatives of acetoacetic ester proceeds more slowly than with the primary isomer. (Despite the lengthy heating of the reaction mixtures, a considerable portion of the initial products was in all cases found unchanged).

The speed of the ester cleavage of the disubstituted derivatives of acetoacetic ester formed in the latter case is obviously greater than the speed of its formation; the corresponding products of reaction tend to be mostly cleavage products - esters of the disubstituted acetic acid.

All the reactions described were carried out in the presence of an excess of methoxychlorpentenes in the reaction medium; in the presence of an excess of sodium and long-continued heating of the reaction mixture, in the case of primary methoxychlorpentene, there was ascertained the formation of a considerable quantity of the cleavage product of the disubstituted acetoacetic ester.

The tendency towards ester cleavage of the disubstituted acetoacetic esters obtained was confirmed by heating the compounds in alcohol solution in the presence of sodium ethylate or sodium alkylacetoacetic ester.

In the course of 2 to 3 hours of heating in the presence of an equimolecular

quantity of sodium ethylate or sodium alkylacetoacetic ester, the cleavage of the disubstituted acetoacetic esters went to completion, while with a small quantity ($1/5$ to $1/4$ the equimolecular quantity) the cleavage was 50 to 60% completed.

The cleavage of the simplest disubstituted derivatives of acetoacetic ester in alcoholic medium in the presence of sodium ethylate has also been observed by Deickman [3]. From dimethylacetoacetic ester he obtained the ester of isobutyric acid.

We further studied the action of secondary methoxychlorpentene on sodium ethylacetoacetic ester in an ether-benzene solution. In this case, the possibility of cleavage of the disubstituted derivatives of the acetoacetic ester formed was excluded. From the reaction, there was obtained in small yield (about 18%) ethyl-n-methoxypentenyl acetoacetic ester. The greater part of the starting materials was found unchanged.

The reaction of secondary methoxychlorpentene with sodium ethylacetoacetic ester in ether-benzene solution took place, accordingly, with a complete allyl rearrangement.

One of the disubstituted acetoacetic esters obtained - butyl-n-methoxypentenyl acetoacetic ester - underwent ketonic cleavage.

The cleavage took place under significantly more rigorous conditions than in the case of the monosubstituted acetoacetic esters [1].

Upon intensive mixing of the ester with 10% KOH no splitting took place either at room temperature or upon heating (100°). During the heating of the ester with an aqueous alcohol solution of KOH there took place simultaneously ketonic and acid cleavage. 3-Methyl-8-methoxyoctene-5-one-2 was isolated in 51% yield. B.p. $145-146^\circ$ (17 mm); n_D^{20} 1.4460; d_4^{20} 0.8942. 1-Methoxydecene-3-carboxylic acid-6 was obtained in 21% yield. B.p. 165° (8 mm); n_D^{20} 1.4510; d_4^{20} 0.9493.

Finally, the reaction between Na-ethylacetoacetic ester and n-octylchloride was studied. On the basis of the results obtained in the present work, we could assume that as a consequence of the insignificant mobility of the chlorine in octylchloride, the reaction would go at about the same speed as in the case of secondary methoxychlorpentene and consequently, slower than the ester cleavage of the ethyloctylacetoacetic ester formed. Consequently, we could expect that the reaction products would include not ethyloctylacetoacetic ester, but the product of the ester cleavage of the latter - the ethyl ester of ethyl octyl acetic acid.

In actuality, when the indicated reaction was carried out, it was found that the reaction between octylchloride and Na-ethylacetoacetic ester went very slowly, and led to the formation of only a single product - the ethyl ester of ethyl octyl acetic acid. B.p. $107-110^\circ$ (3 mm); n_D^{20} 1.4325; d_4^{20} 0.8701. The yield of product under the conditions of the experiment (5 hours of heating) was small, and a considerable part of the starting materials was found unchanged.

We may assume that in other analogous cases as well, when the disubstituted derivatives of acetoacetic ester are used for synthesis with halide derivatives containing almost immobile halogens (alkyl chlorides, presence of steric hindrance, etc.) there will be obtained not the normal products of reaction, but products of their ester cleavage - disubstituted derivatives of the ethyl ester of acetic acid.

This point must also be kept in mind in the synthesis of monosubstituted derivatives of acetoacetic ester, although here it is of less importance, as the

monosubstituted derivatives of acetoacetic ester undergo ester cleavage much more slowly in comparison with the disubstituted derivatives.

EXPERIMENTAL

Action of Mg-acetoacetic Ester on 1-Methoxy-5-chloropentene-3

In a flask with a reflux condenser there were mixed 2.5 g of magnesium, 13 g of acetoacetic ester, and 20 g absolute ethyl alcohol. To stimulate reaction of the mixture, which had been heated to the boiling point, there were added a few drops of carbon tetrachloride. The solution of the Mg took place very vigorously, and was complete in a few minutes. To the resulting solution there was added 15 g of 1-methoxy-5-chloropentene-3, and the mixture was heated on the water bath for 3 hours. The alcohol was then distilled off, the residue extracted with water and hydrochloric acid; the oily layer which separated out was removed and combined with the ether extract obtained by extraction of the lower layer. The ether extract was dried over calcium chloride, the ether distilled off, and the residue distilled in vacuum. There was obtained 4.7 g of the ethyl ester of 1-methoxy-octene-3-one-7-carboxylic acid-6, with B.p. 151-153° (13 mm); n_D^{20} 1.4511; d_4^{20} 1.0040.

Action of 1-Methoxy-5-chloropentene-3 on Na Methylacetoacetic Ester

3.5 g of sodium was dissolved in 43 g of absolute alcohol and then, with cooling, there were added 22 g of methylacetoacetic ester and 20 g of 1-methoxy-5-chloropentene-3. The mixture was heated on the water bath for 3 hours. After distillation of the alcohol, the residue was treated with water until the sodium chloride precipitate was completely dissolved. The upper layer was separated and added to the ether extract obtained from the aqueous solution. After drying of the ether extract over calcium chloride and removal of the ether by distillation, the residue was distilled in vacuum from a small flask with a spiral Widmer column. After several distillations there was obtained 1.8 g of the ethyl ester of 1-methoxyheptene-3-carboxylic acid-6. Its constants are given in Table 2 (formula 1).

0.0772 g substance: 0.1872 g CO₂; 0.0694 g H₂O.

0.1110 g substance: 0.2676 g CO₂; 0.1006 g H₂O.

Found %: C 66.13, 65.75; H 9.98, 9.93.

C₁₁H₂₀O₃. Calculated %: C 66.00; H 10.00.

In addition, there was obtained 28.4 g of the ethyl ester of 3-methyl-8-methoxy-octene-5-one-2-carboxylic acid-3. Constants are given in Table 1 (formula 1).

0.1391 g substance: 0.3293 g CO₂; 0.1142 g H₂O.

Found %: C 64.56; H 9.12.

C₁₃H₂₂O₄. Calculated %: C 64.46; H 9.09.

Action of 1-Methoxy-3-chloropentene-4 on Na-methylacetoacetic ester

An alcohol solution of Na methylacetoacetic ester was prepared from 7.6 g sodium, 76 g absolute alcohol and 45 g methylacetoacetic ester. To the solution was added 45 g 1-methoxy-3-chloropentene-4, and the reaction mixture then heated for 5 hours on the water bath. The alcohol was distilled off, and the residue treated with water and ether. After distillation of the reaction products, there were separated out 33 g of a mixture of the initial reagents; 15.1 g of the ethyl ester of 1-methoxyheptene-3-carboxylic acid-6 (Table 2, formula 1), and 2.1 g of the ethyl ester of 3-methyl-2-methoxyoctene-5-one-2 carboxylic acid-3 (Table 1, formula 1).

* In this case and also in others of a similar nature, the mixture of initial reagents contains a small quantity of products of the 'ester' cleavage of the monoalkyl acetoacetic ester used in the reaction - the ethyl ester of the corresponding fatty acid.

Cleavage of the Ethyl Ester of
3-Methyl-8-methoxyoctene-5-one-2-carboxylic Acid-3

0.2 g of sodium was dissolved in 15 ml of absolute alcohol and to the solution obtained was added 6 g of the ethyl ester of 3-methyl-8-methoxyoctene-5-one-2-carboxylic acid-3. The mixture was heated for 2 hours on a water bath, the alcohol was then driven off, and the residue separated by means of water and ether extraction. After drying of the ether extract and distillation of the ether, the residue was distilled in vacuum from a small flask with a Widmer dephlegmator. There was obtained 2.8 g of the ethyl ester of 1-methoxyheptene-3-carboxylic acid-6 (table 2, formula 1) and about 2 g of the initial ester.

Action of 1-Methoxy-5-chlorpentene-3 on Na-ethylacetoacetic Ester

4.3 g of sodium was dissolved in 70 g of absolute ethyl alcohol and cooled while 30 g ethylacetoacetic ester and 30 g of 1-methoxy-5-chlorpentene-3 were added. The mixture was heated 2 hours on a boiling water bath. Then the alcohol was distilled off, and the residue worked up with water and ether. After distillation of the reaction products there were obtained about 17 g of a mixture consisting of the initial reagents, 1.7 g of a fraction boiling with the range 115-132° (17 mm), n_D^{20} 1.4400, and 32 g of the ethyl ester of 3-ethyl-8-methoxyoctene-5-one-2-carboxylic acid-3, whose constants are given in Table 1 (formula 2).

0.0997 g substance: 0.2395 g CO₂; 0.0852 g H₂O.

Found %: C 65.53; H 9.50.

C₁₄H₂₄O₄. Calculated %: C 65.62; H 9.37.

Action of 1-Methoxy-3-chlorpentene-4 on Na ethylacetoacetic Ester

Na ethylacetoacetic ester was prepared from 4.3 g sodium, 30 g ethylacetoacetic ester, and 70 g ethyl alcohol. Then there was added to the mixture 30 g of 1-methoxy-3-chlorpentene-4, after which it was heated on the water bath for 5 hours. After working up the distillate obtained from the reaction mixture, there were obtained 32.3 g of initial reagents, and 11.3 g of the ethyl ester of 1-methoxyoctene-3-carboxylic acid-6, with constants shown in Table 2, formula 2.

0.1053 g substance: 0.2587 g CO₂; 0.0997 g H₂O.

0.0889 g substance: 0.2195 g CO₂; 0.0977 g H₂O.

Found %: C 67.01; 67.35; H 10.52, 10.31.

C₁₂H₂₂O₃. Calculated %: C 67.29; H 10.28.

Also, 0.9 g of the ethyl ester of 3-ethyl-8-methoxyoctene-5-one-2 carboxylic acid-3, with b.p. 160° (11 mm); n_D^{20} 1.4525.

Action of 1-Methoxy-3-chlorpentene-4

on Na Ethylacetoacetic Ester in Benzene Solution

To 100 ml of absolute ether there were added 3 g of sodium and then, gradually, 20 g of ethylacetoacetic ester. After solution of the sodium, there were added to the solution 22 g of 1-methoxy-3-chlorpentene-4 and 50 ml of absolute benzene. The ether was distilled off and the benzene solution heated on a water bath for 5 hours. After distillation of the benzene, the residue was treated with water and ether. The ether extract was dried over calcium chloride, the ether distilled off, and the residue distilled in vacuum. After distilling off the chloride and the ethylacetoacetic ester which had not reacted, there came over 1.1 g of a fraction boiling in the range 128-160° (16 mm; n_D^{20} 1.4460, and 6 g of the ethyl ester of 3-ethyl-8-methoxyoctene-5-one-2-carboxylic acid-3, with b.p. 163° (14 mm); n_D^{20} 1.4520.

Cleavage of the Ethyl Ester of 3-Ethyl-8-methoxy-
octene-5-one-2-carboxylic acid-3

Experiment 1. 15 g of the ester was added to a solution of 1.5 g sodium in 30 ml of absolute alcohol. The mixture was heated for 2 hours on a water bath. Upon working up and distilling the reaction mixture there were obtained 7.8 g of the ethyl ester of 1-methoxyoctene-3-carboxylic acid-6 with b.p. 120-121° (12 mm); n_D^{20} 1.4380; d_4^{20} 0.9282, and 1.2 g of the initial ester.

Experiment 2. 10.3 g of ester, 0.3 g of sodium and 20 ml of alcohol were heated for 3 hours. There was obtained 3.1 g of the ethyl ester of 1-methoxyoctene-3-carboxylic acid-6.

Action of 1-Methoxy-5-chloropentene-3 on Na Propylacetoacetic Ester

5 g of sodium was dissolved in 60 g of absolute alcohol and to the solution after cooling, there were added 33 g propylacetoacetic ester and 32 g 1-methoxy-5-chloropentene-3. The mixture was heated on a water bath for 3 hours. After distilling off the alcohol, working up the residue with water and ether, drying, and distilling off the ether, there was obtained a residue which was distilled from a flask with a Widmer dephlegmator. There were separated 2.2 g of the ethyl ester of 1-methoxynonene-3-carboxylic acid-6 with b.p. 114° (4 mm); n_D^{20} 1.4400; d_4^{20} 0.9225 and 39.6 g of the ethyl ester of 3-propyl-8-methoxyoctene-5-one-2-carboxylic acid-3, whose constants are given in Table 1 (formula 3).

Bromination by the method of MacIlliny. 0.490 g of material combined with 0.38 g Br₂; theoretically, 0.34 g Br₂ was required.

0.0967 g substance: 0.2354 g CO₂; 0.0843 g H₂O.

0.0903 g substance: 0.2204 g CO₂; 0.0806 g H₂O.

Found %: C 66.39, 66.57; H 9.68, 9.91.

C₁₅H₂₈O₄. Calculated %: C 66.66; H 9.63.

Action of 1-Methoxy-3-chloropentene-4 on Na Propylacetoacetic Ester

Na propylacetoacetic ester was prepared from 5 g sodium, 38 g propylacetoacetic ester, and 71 g absolute alcohol. After the addition of 40 g of 1-methoxy-3-chloropentene-4, the mixture was heated on a water bath for 5 hours. Upon distillation of the reaction mixture there were separated 33.4 g of the initial reagents and 12.8 g of the ethyl ester of 1-methoxynonene-3-carboxylic acid-6, whose constants are given in Table 2 (formula 3).

0.6821 g substance: combined with 0.40 g Br₂; theoretically, 0.48 g Br₂ necessary.

0.0750 g substance: 0.1882 g CO₂; 0.0730 g H₂O.

0.0825 g substance: 0.2054 g CO₂; 0.0814 g H₂O.

Found %: C 68.44, 67.91; H 10.82, 10.95.

C₁₃H₂₄O₃. Calculated %: C 68.42; H 10.53.

Action of 1-Methoxy-5-chloropentene-4 on Na Butylacetoacetic Ester

5 g of sodium was dissolved in 80 g of absolute alcohol, and 40 g of butylacetoacetic ester and 35 g of 1-methoxy-5-chloropentene-3 were added to the solution. The mixture was heated on a water bath for 5 hours. Upon working up and distilling the reaction mixture, there were obtained 1.8 g of a fraction boiling from 144-146° (13 mm); n_D^{20} 1.4403, and 39.4 g of the ethyl ester of 3-butyl-8-methoxyoctene-5-one-2-carboxylic acid-3 (constants in Table 1, formula 4).

0.1244 g substance: 0.3076 g CO₂; 0.1146 g H₂O.

Found %: C 67.44; H 10.23.

C₁₈H₂₈O₄. Calculated %: C 67.60; H 9.86.

Action of 1-Methoxy-3-chloropentene-4 on Na Butylacetoacetic Ester,

Na butylacetoacetic ester was prepared from 5 g of sodium, 40 gm of butyl acetoacetic ester, and 80 g of absolute alcohol. To the solution was added 35 g of 1-methoxy-3-chloropentene-4, and the mixture was then heated for 6 hours on a water bath. Upon working up and distilling the reaction mixture, there were separated out 25.7 g of the initial reagents and 26.4 g of the ethyl ester of 1-methoxydecene-3-carboxylic acid-6; its constants are in Table 2 (formula 4).

0.7460 g substance: combined with 0.43 g Br₂; theoretically required Br₂ - 0.49 g.

0.6270 g substance: combined with 0.32 g Br₂; theoretically required Br₂ - 0.41 g.

0.1274 g substance: 0.3230 g CO₂; 0.1209 g H₂O.

0.1360 g substance: 0.3452 g CO₂; 0.1294 g H₂O.

Found %: C 69.14, 69.28; H 10.55, 10.57.

C₁₄H₂₆O₃. Calculated %: C 69.42; H 10.74.

Ketone Cleavage of the Ethyl Ester of 3-Butyl-8-methoxyoctene-5-one-2-carboxylic acid-3

Experiment 1. 4 g KOH was dissolved in 50 ml of water and 10 g of ester added to the solution. The mixture was stirred vigorously by a mechanical stirrer for 3 hours at room temperature and then for 4 hours while being heated on a water bath. The mixture was extracted with ether, the ether extract dried, the ether distilled off, and the residue distilled from a small flask. There was separated 9.3 g of the initial ester with a b.p. of 176° (14 mm). The aqueous solution was acidified with sulfuric acid and extracted with ether. After driving off the ether, no residue was observed in the flask.

Experiment 2. 10 g of the compound was vigorously stirred with 50 ml of 10% sulfuric acid for 4 hours while being heated on a water bath. Upon working up the reaction mixture, 9.6 g of the initial ester was obtained.

Experiment 3. 3 g of KOH was dissolved in an alcoholic solution containing 20 g of water and 50 g of methyl alcohol. To the resultant solution 9.3 g of ester was added, and the reaction mixture then heated on the water bath for 3 hours. The alcohol was then driven off, the residue extracted with ether, the ether extract dried with calcium chloride, the ether driven off, and the residue distilled in vacuum. There was obtained 3.6 g of 3-methyl-8-methoxyoctene-5-one-2:

B.p. 145-146° (17 mm); n_D^{20} 1.4460; d_4^{20} 0.8942.

Found: MR_D 63.22.

C₁₃H₂₄O₂F. Calculated: MR_D 63.42.

0.0997 g substance: 0.2682 g CO₂; 0.0998 g H₂O.

Found %: C 73.36; H 11.12.

C₁₃H₂₄O₂. Calculated %: C 73.58; H 11.32.

The remaining water was later acidified with sulfuric acid and extracted with ether. Upon driving off the ether and distilling the residue, there was obtained 1.7 g 1-methoxydecene-3-carboxylic acid-6.

B.p. 165° (8 mm); n_D^{20} 1.4510; d_4^{20} 0.9493

Found: MR_D 60.69.

C₁₂H₂₂O₃F. Calculated: MR_D 60.33.

0.0955 g substance: 0.2364 g CO₂; 0.0890 g H₂O.

Found %: C 67.50; H 10.36.

C₁₂H₂₂O₃. Calculated %: C 67.29; H 10.28.

Cleavage of the Ethyl Ester of 3-Butyl-8-methoxyoctene-5-one-2-
-carboxylic Acid-3, in Alcohol Solution of the Alcoholate

0.2 g of sodium was dissolved in 25 ml of absolute alcohol and to the solution was added 15 g of ester. The mixture was heated on the water bath for 3 hours. Upon working up and distilling the reaction mixture, there were separated 8.3 g of the ethyl ester of 1-methoxydecene-3-carboxylic acid-6 (Table 2, formula 4) and 5.4 g of the initial ester.

Oxidation of the Ester of 3-Butyl-8-methoxyoctene-5-
one-2-carboxylic acid-3 with potassium permanganate

15 g of the ester was added to 500 g of water, and then to the mixture, with continuous stirring, there was gradually added 20 g of powdered potassium permanganate. After standing for a day over manganese dioxide, the solution became colorless and transparent. The manganese dioxide was filtered off and carefully washed with hot water. The filtrate was concentrated almost to dryness, acidified with dilute sulfuric acid, and extracted with ether. The ether extract was dried over calcium chloride, the ether driven off, and the residue distilled in vacuum. There was obtained 2.6 g of methoxypropionic acid with b.p. 106°-107° (13 mm); n_D^{20} 1.4170.

Oxidation of the Ethyl Ester of 1-Methoxydecene-3-
-carboxylic Acid-6 with Potassium Permanganate

To a mixture of 15 g of ester and 500 g of water there was gradually added, during cooling with water and continuous stirring, powdered potassium permanganate.

In all there was added 23 g of permanganate. The mixture was set aside to stand for a day. The solution lost its color. The manganese dioxide was filtered off and washed with hot water. The filtrate was concentrated to dryness, acidified with sulfuric acid, and extracted with ether. After driving off the ether and distilling, there were obtained 3.1 g of methoxypropionic acid with b.p. 107°-110° (14 mm); n_D^{20} 1.4178, and 8.2 g of the ethyl ester of butylsuccinic acid:

B.p. 140-142° (4 mm); n_D^{20} 1.4424; d_4^{20} 1.0510.

Found MR_D 50.90.

C₁₀H₁₈O₄. Calculated MR_D 51.45.

0.1045 g substance: 0.2286 g CO₂; 0.0790 g H₂O.

Found %: C 59.66; H 8.40.

C₁₀H₁₈O₄. Calculated %: C 59.41; H 8.91.

Action of Octyl Chloride on Na Ethylacetoacetic Ester

To the alcohol solution of Na ethylacetoacetic ester obtained from 15 g ethylacetoacetic ester, 2 g sodium, and 35 g ethyl alcohol, was added 16 g of n-octyl chloride. The mixture was heated on the water bath for 5 hours. Upon working up and distilling the reaction mixture, there were obtained about 20 g of a mixture of the initial reagents and 2.3 g of the ethyl ester of ethyloctylacetic acid:

B.p. 107-110° (3 mm); n_D^{20} 1.4325; d_4^{20} 0.8701.

Found: MR_D 68.50.

C₁₄H₂₈O₂. Calculated: MR_D 68.03.

0.1112 g substance: 0.2992 g CO₂; 0.1210 g H₂O.

Found %: C 73.38; H 12.10.

C₁₄H₂₈O₂. Calculated %: C 73.68; H 12.28.

SUMMARY

1. The reactions between primary methoxychlorpentene and Na derivatives of methyl-, ethyl-, propyl-, and butylacetoacetic esters proceed normally, without rearrangements, and lead to the formation of the corresponding disubstituted derivatives of acetoacetic ester.

2. As the result of the reaction between secondary methoxychlorpentene - 1-methoxy-3-chlorpentene-4 - and the Na derivatives of the methyl-, ethyl-, propyl-, and butylacetoacetic esters, there are formed either as chief products of the reaction or exclusively, the esters of the disubstituted acetic acids.

3. It has been established that the esters of the disubstituted acetic acid are formed as a result of the ester cleavage of the disubstituted derivatives of acetoacetic ester in the presence of sodium ethylate or Na alkylacetoacetic ester and alcohol.

The speed of formation of the disubstituted acetoacetic esters in the case of secondary methoxychlorpentene depends upon the slow monomolecular reaction of dissociation of the chloride into ions, which is considerably slower than the reaction of ester cleavage of the disubstituted derivatives of acetoacetic ester formed.

The reaction of secondary methoxychlorpentene takes place with a complete allyl rearrangement.

4. It has been shown that the disubstituted derivatives of acetoacetic ester undergo ester cleavage upon heating with sodium ethylate in alcoholic medium.

5. As a result of the reaction between n-octylchloride and Na-ethylacetoacetic ester there is obtained a product of the ester cleavage of the ethyl ester of ethyloctylacetoacetic acid first formed - the ethyl ester of ethyloctylacetic acid.

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Received January 6, 1948.

ON THE ORDER OF ADDITION OF ALKYLHYPOHALITES TO DIVINYL

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In a series of articles, published chiefly in this journal, the author has described the results of experiments on the order of addition of hypohalite compounds to various diene hydrocarbons and their derivatives [1]. These investigations have led to the conclusion that hypohalite derivatives add to dienes having conjugated double bonds in the 1,2 position, whereas halides and halide hydrocarbons add to the same compounds chiefly in the 1,4 position.

Inasmuch as the conclusion arrived at was of undoubted theoretical interest and opened new possibilities for organic synthesis, several authors continued these investigations with new objectives and under changed conditions. As a result of these new investigations with considerably greater quantities of starting materials than were at the disposal of the author of this paper, it was found that as the result of the addition of hypochlorous acid and alkyl hypochlorites to divinyl, there were formed along with the 1,2 products the 1,4 products as well, although in considerably smaller amounts. Thus, for example, in the reaction of benzosulfodichloramide with a solution of divinyl in ethyl alcohol, according to the data of B.A. Arbuzov and V.M. Zoroastrova [2], about 12% of the 1,4 product is formed. In the reaction of chlorine and ethylene oxide with divinyl, 38% of the 1,4 chloroether is formed [3]. Upon treating divinyl with bleaching powder and carbon dioxide, the content of 1,4-chlorhydrin in the mixture reaches 27% [4]. Much earlier, the formation of small quantities of 1,4 product was also observed upon addition of hypochlorous acid to cyclohexadiene-1,3 [5]. On the other hand, during the determination of the order of addition of hypobromous and hypoiodous derivatives to divinyl, the 1,4 products have thus far never been observed at all [6].

The appearance of these new investigations on the hypohalogenation of divinyl caused the author once more to consider the question of the order of addition of hypohalite compounds to conjugated systems, and first of all to divinyl, with the object of clarifying the conditions favoring 1,2 or 1,4 addition. In a preliminary communication on this subject, it was shown that the decisive influence on the order of addition was exercised by the temperature at which the reaction took place, and the amount of heat liberated in the process, [7]. This conclusion completely corresponds to the fact that 1,4 products are thermodynamically more stable, and are formed from 1,2 products under conditions guaranteeing sufficient mobility of the system. 1,2 addition, in the author's opinion, is a consequence of the influence of kinetic, and not of thermodynamic factors.

In the investigation in question, the object was to explain in greater detail the influence upon the order of addition of the following factors: 1) the nature of the halogen; 2) the size of the alkyl radical; 3) temperature; 4) the duration of the reaction; 5) the method of hypohalogenation.

In order to explain the influence upon the order of addition of the nature of the halogen, an investigation was made, under identical conditions, of the action upon alcohol solutions of divinyl of benzosulfodichloramide,

benzosulfodibromamide, and iodine plus mercuric oxide. In these experiments, the formation of 1,4 products was confirmed only in the first case. In the second and third cases only the formation of 1,2 products was observed, along with small quantities of the products of addition to divinyl of two molecules of alkylhypohalogenite.

The accuracy of the experiments was such that 5% of the 1,4 product would have been detected with certainty.

Thus, the nature of the halogen shows an actual influence upon the order of addition of alkylhypohalogenites. In the case of chlorine, there indisputably takes place, along with 1,2 addition, 1,4 addition. In the case of the other halogens, either the reaction does not take place at all, or it proceeds to a negligibly small degree.

In order to make clear the influence upon the order of addition of the size of the alcohol radical which forms part of the alkylhypohalogenite, experiments were arranged on the action of benzosulfochloramide upon solutions of divinyl in methyl, ethyl, and n-butyl alcohols at the same temperature and concentration of the solution. These experiments showed that in the case of addition of methylhypochlorite, the yield of 1,4 product was considerably lower than in the case of ethylhypochlorite. At the same time, the change in the ratio of yields of isomeric chlorethers in the passage from ethyl alcohol to butyl was not great.

The nature of the alcohol also shows a strong influence upon the total yield of chlorether. With an increase in size of the alkyl radical, the total yield of chlorether falls sharply, while the yield of that addition product of the dichloramide with divinyl which contains active chlorine increases greatly. Although during the action of the dichloramide upon a solution of divinyl in methyl alcohol at a temperature of about -10° the formation of an addition product with active chlorine hardly takes place at all, in the case of butyl alcohol under the same conditions, the yield of this same material reaches 70%. The yield of monochlorether at the same time falls from 46.5 to 6.4%. Thus, the size of the alcohol radical shows a genuine influence both upon the order of addition, and upon the yield of chlorether.

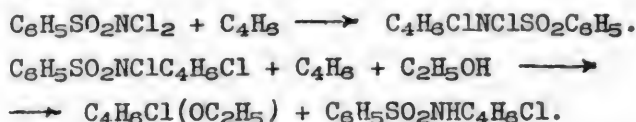
To clarify the influence of temperature upon the order of addition of alkylhypohalogenites upon divinyl, experiments were arranged for the reaction of benzosulfodichloramide upon solutions of divinyl in methyl, ethyl, and butyl alcohols at temperatures from -12 to 8° , and $+35$ – 45° . In the first two cases, there was observed a sharp increase in yield of 1,4 chlorether upon the increase in temperature. In methyl alcohol, the yield of chlorether rose from 17 to 30%, in ethyl alcohol from 5 to 20%. In butyl alcohol, no such clear picture was obtained, because of the fact that at -10° the yield of ether in this case was very small, and it was impossible to determine accurately the proportion of isomeric chlorethers in the product.

A change in the temperature of reaction shows an actual influence also upon the total yield of chlorethers. The yield of methyl chlorether changed little with an increase in temperature. The yields of ethyl and butyl chlorethers increased sharply with the increase in temperature (in the interval shown, 2 and 3 times, respectively). It must also be pointed out that with the increase in temperature there was a sharp decrease in the yield of secondary products – those products of the addition of dichloramide to divinyl which contain active chlorine.

The experiments set up to show the influence upon the order of addition of continuous mixing of the reaction mixture indicated that this influence was either non-existent or small. At the same time, these experiments permitted the

drawing of interesting conclusions with regard to the mechanism of the action of benzosulfodichloramide upon alcoholic solutions of divinyl. It was shown that under these conditions the formation of chlorethers proceeds along two different paths, the importance of each of these paths depending upon the temperature. At a temperature of about -10° , the dichloramide, upon addition to the reaction mixture, quickly reacts with the divinyl, forming an addition product containing active chlorine. If at the given temperature the dichloramide is added to the reaction mixture comparatively quickly, and then this addition product is removed, the yield of chlorethers is negligibly small. Thus, for example, upon decreasing the time of carrying out the reaction from 6 to 2 hours, the yield of chlorethers in the case of ethyl alcohol is decreased to a third. At the same time, the yield of the addition product of dichloramide with divinyl, containing active chlorine, increased from 12 to 65%.

Thus, these experiments have shown that the reaction of benzosulfodichloramide with alcohol solutions of divinyl proceeds, under these conditions, to a considerable degree in two steps: first there takes place the addition of the dichloramide to divinyl, with the formation of an addition product containing active chlorine, and then this product acts upon the alcohol solution of divinyl with the formation of chlorethers.



This observation modifies earlier views on the mechanism of the formation of addition products of chloramide with olefins in the reaction of benzosulfodichloramide with alcohol solutions of olefins, expressed by M.V. Likhoshesterov [8]. The latter assumed that first the dichloramide acted upon the alcohol by means of one of its chlorine atoms with the formation of a chlorether, and that then the product quickly combined with the olefin with the formation of an addition product without active chlorine. Our experiments have shown that such an assumption, at least in the case of divinyl, does not correspond with reality.

The path of reaction here considered is not the only one, even at low temperatures. Among the products of the reaction of dichloramide with alcoholic solutions of divinyl there is always free amide, which can be formed from dichloramide only by the reaction:



Upon raising the temperature, this second path of the reaction becomes the predominant one. At a higher temperature, the yield of addition product containing active chlorine falls sharply, and the yield of amide increases.

The importance of each of these two paths of formation of chlorethers depends, obviously, also upon the nature of the alcohol, as the yield of addition product containing active chlorine increases, while the yield of amide decreases, as we pass from methyl to ethyl and butyl alcohols.

The results given with regard to the mechanism of the reaction of benzosulfodichloramide with alcoholic solutions of olefins make comprehensible the fact that the yields of chlorethers resulting from this reaction almost never surpass 50%. As a rule, the yield is of the order of 30 to 40% [9].

In order to make clear the influence upon the order of addition of alkylhypohalites of the method of carrying out the reaction, parallel experiments were arranged for the action upon solutions of divinyl in ethyl alcohol (at identical temperatures and concentrations of benzosulfodichloramide) of tertiary butyl

hypochlorite, and chlorine plus alcoholate. In the case of the dichloramide, the yield of 1,4 chlorether was 5 to 6%, in the case of butylhypochlorite 12%, and in the last case, 25%.

The increase in yield of the 1,4 product in the second case was possibly related to the fact that in order to speed up the reaction, the mixture was subjected to radiation from a quartz lamp. As for the action of chlorine and alcoholate upon the alcohol solution of divinyl, here the increased yield of 1,4 chlorether is probably related to the presence of a secondary reaction. Along with the chlorethers, there is formed under these conditions a large quantity of 1,4 dichloride, which, as direct experiment shows, is capable of entering into a substitution reaction with alcoholates, with the formation of 1,4 chloroethers. In the same manner, 1,2 dichlorbutene-3 and alcoholic alkali give chloroprene [10].

Thus, this fourth comparison of experimental data has shown that the method of carrying out the addition of alkylhypochlorites to divinyl also influences the order of addition, apparently, however, because of secondary processes.

Of the 1,2 halogen ethers with which we have had to deal in this investigation, the ethyl chlor- and brom- ethers, as well as all the iodo- ethers, have been described by the author of this paper in earlier communications. Methyl and butyl chlorethers are described first. For the products described earlier, more precise constants are here given, and misprints which could not be corrected previously are here corrected. Of the 1,4-chlorethers, only the ethyl ether [11] was described previously. The 1,2 chlorethers are colorless liquids with an agreeable odor, specific for each ether. The 1,4 ethers have not a strong, but a sharp odor, related to the presence in the molecules of allyl chloride. The 1,2 iodo ethers have a sweetish, cloying odor. Upon storing, they are gradually discolored by the separation of iodine with a brown color. The constants of the chlor- and iodo-ethers described in this work are given in Table 1.

Table 1

Formula	Boiling point	P (in mm)	d_4^{20}	n_D^{20}	MR _D	
					calc.	Found
CH ₂ Cl-CH(OCH ₃)-CH=CH ₂	123.5-124.5°	755	1.0041	1.4342	31.33	31.28
CH ₂ Cl-CH(OC ₂ H ₅)-CH=CH ₂	136-136.5°	740	0.9706	1.4320	35.95	35.98
CH ₂ Cl-CH(OC ₄ H ₉)-CH=CH ₂	76.5-77.5°	20	0.9440	1.4380	45.19	45.23
CH ₂ Cl-CH=CH-CH ₂ OCH ₃	151-153°	760	1.0246	1.4528	31.33	31.79
CH ₂ Cl-CH=CH-CH ₂ OC ₂ H ₅	62-64	15	0.9912	1.4518	35.95	36.62
CH ₂ Cl-CH=CH-CH ₂ OC ₄ H ₉	95-100	20	0.9544	1.4498	45.19	46.00
CH ₂ I-CH(OCH ₃)-CH=CH ₂	64.5	20	1.6178	1.5148	39.27	39.51
CH ₂ I-CH(OC ₂ H ₅)-CH=CH ₂	74	20	1.5296	1.5060	43.88	43.91
CH ₂ I-CH(OC ₃ H ₇)-CH=CH ₂	87-87.5	20	1.4515	1.5000	48.50	48.65

To demonstrate the structure of the isomeric chlorethers, the difference in the nature of their reactions with alcoholic alkali was utilized. While the 1,2-chlorethers give alkoxyrenes in this reaction, the 1,4-chlorethers exchange the chlorine in the alkoxy residue with the formation of the full ethers of erythroglycols.

The constants of the alkoxyrenes obtained from the 1,2 halogen ethers are given in the experimental section, the constants of the diethers of the erythroglycols obtained from 1,4-chlorethers and from 1,4-dibrombutene-2 are given

for comparison in Table 2. In Table 3 are given the constants of the dibromides of these diethers.

Table 2

Formula	Boiling pt. at 20 mm	d_4^{20}	n_D^{20}	MR_D		Method of obtaining
				Calc.	Found	
$CH_3O-CH_2-CH=CH-CH_2OCH_3$	48-50°	—	1.4238	—	—	from chlor- ether
	50	0.8969	1.4238	32.72	33.04	from di- bromide
$CH_3OCH_2-CH=CH-CH_2OC_2H_5$	62-62.5	0.8840	1.4254	37.35	37.67	from ethyl ether
	62-62.5	0.8829	1.4252	37.35	37.72	from methyl ether
$C_2H_5OCH_2-CH=CH-CH_2OC_2H_5$	72-72.5	—	1.4256	—	—	from chlor- ether
	72-72.5	0.8714	1.4256	41.96	42.36	from di- bromide
$C_4H_9OCH_2-CH=CH-CH_2OC_4H_9$	129-132	0.8598	1.4365	60.44	60.97	from chlor- ether
	131-132	0.8602	1.4365	60.44	60.97	from di- bromide

Table 3

Formula	Temperature		d_4^{20}	n_D^{20}	MR_D		Note
	M.P.	B.P. at 10 mm			Calc.	Found	
$CH_3OCH_2-CHBr-CHBr-CH_2OCH_3$	67-68	108	—	—	—	—	Upper data given for products ob- tained by brominating diethers from dibromides; lower, for bromination of diethers from chlorethers
	67-68	108	—	—	—	—	
$CH_3OCH_2-CHBr-CHBr-CH_2OC_2H_5$	—	114-115	1.5789	1.4960	53.34	53.66	
	—	114-115	—	—	—	—	
$C_2H_5OCH_2-CHBr-CHBr-CH_2OC_2H_5$	28-30	119.5- 120.5	—	—	—	—	
	28-30	119.5- 120.5	—	—	—	—	
$C_4H_9OCH_2-CHBr-CHBr-CH_2OC_2H_5$	—	163	1.3406	1.4821	76.43	76.60	

It is necessary to note that the methyl ethyl ether of erythroglycol was obtained by the action of a solution of alkali in ethyl alcohol upon 1-chlor-4-methoxybutene-2 and by the action of a solution of alkali in methyl alcohol upon 1-chlor-4-ethoxybutene-2.

In Tables 1 and 2, attention is drawn to several values of the molecular refraction found experimentally to be higher than those calculated for 1,4 derivatives. This phenomenon has also been observed with other compounds of similar structure. It is obviously related to the presence of resonance of the type



In addition to the compounds enumerated, dibromides were also obtained

from the chlorethers. The dibromide of ethyl 1,2-chlorether has been described earlier, the others are described for the first time. The constants of the dibromides are given in Table 4.

Table 4

Formula	B.p. at 20 mm	d_4^{20}	n_D^{20}	MRD	
				Calcul.	Found
$\text{CH}_2\text{Cl}-\text{CH}(\text{OCH}_3)-\text{CHBr}-\text{CH}_2\text{Br} \dots$	124.5-125.5°	1.8362	1.5286	47.33	47.32
$\text{CH}_2\text{Cl}-\text{CH}(\text{OC}_2\text{H}_5)-\text{CHBr}-\text{CH}_2\text{Br} \dots$	129	1.7232	1.5182	51.95	51.80
$\text{CH}_2\text{Cl}-\text{CH}(\text{OC}_4\text{H}_9)-\text{CHBr}-\text{CH}_2\text{Br} \dots$	153.5-154.5	1.5753	1.5071	61.18	60.93
$\text{CH}_2\text{Cl}-\text{CHBr}-\text{CHBr}-\text{CH}_2\text{OCH}_3 \dots$	126.5	1.833	1.5310	47.33	47.32
$\text{CH}_2\text{Cl}-\text{CHBr}-\text{CHBr}-\text{CH}_2\text{OC}_2\text{H}_5 \dots$	130-132	1.7063	1.5174	51.95	52.24

The experiments described in this paper permit us to conclude definitely that alkylhypohalogenites add to divinyl exclusively or chiefly in the 1,2 position, that is, in a manner opposite to that of the halogens, which give chiefly the 1,4 products. Consequently, the hypothesis suggested earlier is essentially confirmed. The experiments of B.A. Arbuzov have led to no new conclusions with regard to this. If the author of the present article in his much earlier work did not isolate a single 1,4 product, that is to be explained by his small yields under the conditions in which he worked (small quantities of divinyl, low temperature of carrying out the reaction). Thus the question of the causes for the specific behavior of hypohalogenite compounds in addition reactions with conjugated systems requires essentially the same answer as before.

As has already been noted in an earlier communication, the author sees no decisive reasons for departing from the point of view expressed previously, and considers, as before, that the 1,2 addition of hypohalite compounds to conjugated systems is related to steric factors, that is, is the consequence of the action of kinetic, and not of thermodynamic factors.

1. If we assume that in all the reactions studied there are first formed free alkylhypohalogenites, which then add according to the position of the double bond, then their predominant addition in the 1,2 position may be related to the comparatively small dimensions of the oxygen atom in comparison with the halogen atoms.

In the series iodine - bromine - chlorine hypohalogenites, as can be seen from Table 5, the yield of 1,4 products decreases and the yield of 1,2 products increases. Simultaneously, there is a decrease in this series of the dimensions of the negatively polarized part of the molecule that adds on.

On the basis of the combination of these two facts, we assumed in earlier work [1] that at the first moment of reaction of divinyl with various molecules to be added, there is a coordination of the positively polarized part of the addend with the most negatively polarized atom of the divinyl, the entry of the negatively polarized part of the addend in the two or four position depending on the steric probability that this part will fall into the sphere of activity of the second or fourth carbon atom, i.e., it is determined by the dimensions of this part. From this point of view, the character of the change of the order of addition in the series indicated above becomes comprehensible.

The experimental data with regard to the order of addition of halogens, hydrogen halides, and hypohalogenites to other diene hydrocarbons and halogen derivatives confirms this conclusion about the role of the steric factor [1].

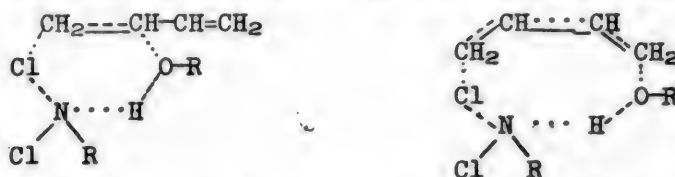
Table 5

Addend	Percent		Covalent radius of the negatively polarized atom
	1,2 product	1,4 product	
Iodine.....	—	about 100	1.33
Bromine.....	30	70	1.14
Chlorine	45	55	0.99
Hypochlorite.....	65-95	5-38	0.74

2. Numerous objections have been brought against the assumption of intermediate formation of alkyl hypohalogenites in reactions of the type under consideration. The most weighty are based on kinetic data. These indicate the simultaneous participation in the intermediate complex of the hypochlorinating reagent, the olefin, and the alcohol.

The question about the correctness of this new reaction scheme cannot be considered decisively settled. However, if this scheme is shown to be correct, then the predominant 1,2 addition of hypohalite compounds may be explained by the peculiar stability of the intermediate six-membered complex because of resonance of the type of the benzol ring. In the case of addition in the 1,4 position, a less stable eight-membered ring would be formed.

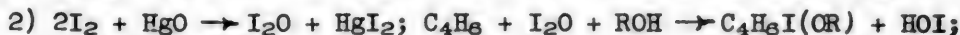
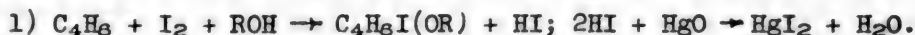
From the point of view of this assumption, the reaction of divinyl with dichloramide and alcohol may be represented in the following manner:



The reaction of divinyl with butylhypochlorite and alcohol, and the reaction of divinyl with chlorine and alcoholate would take place analogously.

Thus, if the theory is shown to be correct, with its denial of the intermediate formation of alkylhypohalogenites, in that case steric factors would be decisive for the order of addition.

The reaction of divinyl with iodine and mercuric oxide in alcoholic solutions may proceed according to two schemes, of which the second appears to us more probable:



Whatever the mechanism of the reaction may be, the increase in the quantity of energy in the intermediate complex on account of the heat of reaction must lead, for evident reasons, to an increased yield of the thermodynamically more stable 1,4 product. Especially therefore in the case of the alkylhypochlorites, which add to olefins with the evolution of a great deal of heat, there takes place the formation of more or less appreciable quantities of 1,4 products, while in the case of the other alkylhypohalogenites, which add to olefins with a smaller evolution of heat, the 1,4 products are practically not formed at all. The greatest yield of 1,4 product was obtained in the reaction of chlorine and ethylene oxide upon divinyl, where the exothermic splitting of the oxygen ring plays a significant role.

EXPERIMENTAL

A. Addition of methylhypohalogenites

1. The reaction of divinyl with benzosulfochloramide in methyl alcohol.

a) To a solution of 68 ml of divinyl (0.75 mole) in 100 ml methyl alcohol (2.5 moles) at minus 12-15°, 63 g of benzosulfodichloramide (0.5 g-equivalent based on 90% activity of dichloramide) was added in small portions over a 4 hour period with mechanical stirring. Stirring at the given temperature was continued for 2 hours. Then the precipitate which had formed was filtered off (7 g; benzo-sulfamide, m.p. 152-153°) and the solution was treated with an excess of powdered sodium sulfite, while stirring was continued and the temperature was maintained at minus 5° or lower. The reaction mixture, now freed of active chlorine, was steam-distilled. The distillate was diluted with water, the reaction product separated, washed with water, and dried over CaCl_2 . A second distillation, and dilution with aqueous alcohol solution of what remained after separating out the reaction product, succeeded in removing an additional small quantity of chlorethers. The total obtained in this manner was 32 g of chlorethers. Upon distillation of the reaction products at ordinary pressure, the following fractions were obtained:

1) Up to 120° - 1.8 g; 2) 120-130° - 20.0 g (1,2-chlorether); 3) 130-140° - 2.0 g; 4) 140-150° - 0.5 g; 5) 150-160° - 4.0 g (1,4-chlorether); 6) 160-170° - 0.4 g; and 7) residue, 2.5 g.

Thus, the yield of monochlorethers constituted about 28 g, 46.5% of theory, basing the calculation upon the amount of active chlorine consumed. The relative amounts of isomeric chlorethers were: 1,2 chlorether - 83%, 1,4 chlorether - 17%.

The first fraction of the reaction products contained small quantities of a substance which from its boiling point (60 to 70°) and its odor might be considered 1-chlorbutadiene. A careful distillation of the second and fifth fractions gave fairly pure 1,2-chlorether (1-chlor-2-methoxybutene-3) and 1,4-chlorether (1-chlor-4-methoxybutene-2), whose constants are given in Table 1).

Analysis of the 1,2-chlorether:

0.1516 g substance: 0.1858 g AgCl .

Found %: Cl 29.33

$\text{C}_5\text{H}_9\text{OCl}$. Calculated %: Cl 29.40.

Analysis of the 1,4-chlorether:

0.1531 g substance: 0.1802 g AgCl .

Found %: Cl 29.11.

$\text{C}_5\text{H}_9\text{OCl}$. Calculated %: Cl 29.40.

The structure of the 1,2-chlorether was shown by its conversion into methoxyprene. Upon boiling 12 g of the 1,2-chlorether for 45 minutes with a twofold excess of alcoholic alkali, there was obtained 6.5 g of methoxyprene with a b.p. 74.5-75.5° and n_D^{20} 1.4475. Yield, 75%. Data found earlier for methoxyprene were: b.p. 74-75.5°, n_D^{20} 1.4442.

By the action of 4 g of bromine in chloroform solution upon 3 g of the 1,2-chlorether at a temperature not above 0°, 6.2 g (yield 88.9%) of 1-chlor-3,4-dibrom-2-methoxybutane was obtained, with constants given in Table 3.

Analysis of the dibromide

0.1824 g substance: 0.3368 g AgCl + 2 AgBr .

Found %: Cl + 2 Br 69.49.

$\text{C}_5\text{H}_9\text{OClBr}_2$. Calculated %: Cl + 2 Br 69.64.

The structure of the 1,4-dichlorether was shown by its conversion into the dimethyl ether of erythroglycol. 3.6 g of the 1,4-dichlorether was heated with a solution of 4.0 g KOH in 15 ml of ethyl alcohol for 30 min. Then 20 ml of water was added to the mixture, and the reaction product extracted with ether. After washing with water and drying over CaCl_2 , the ether was driven off on the water bath, and the reaction product distilled in vacuum. In this way 1.6 g of the dimethyl ether of erythroglycol was obtained, with a b.p. of $48-50^\circ$ at 20 mm and n_D^{20} 1.4236.

The bromination of 1.6 g of this ether in chloroform at minus 10° gave 3 g of dibromide with a b.p. 108° at 10 mm, and m.p. 67° (after repeated recrystallization from alcohol).

0.1674 g substance: 0.2275 g AgBr.

Found %: Br 57.83.

$\text{C}_6\text{H}_{12}\text{O}_2\text{Br}_2$. Calculated %: Br 57.91.

For purposes of comparison, the dimethyl ether of erythroglycol was prepared by the action of a KOH solution in methyl alcohol upon the crystalline 1,4-dibromide of divinyl. To a hot solution of 20 g KOH in 40 ml methyl alcohol with a reflux condenser above, was added 21.4 g of 1,4-dibrombutene-2. After 30 minutes of boiling, the mixture was treated as indicated previously. There was thus obtained 8 g of the dimethyl ether of erythroglycol (yield 70%) with b.p. 50° at 20 mm and n_D^{20} 1.4238. The dibromide of this ether, after recrystallization from alcohol, melted at $66-67^\circ$.

In addition to the dimethyl ether, the methyl ethyl ether of erythroglycol was also prepared from the 1,4-chlorether. 4.7 g of 1,4-chlorether was treated, during heating, with a solution of 3.6 g of KOH in 15 ml of ethyl alcohol. Using the usual procedures, 2.9 g (57.2% yield) of the methyl ethyl ether of erythroglycol was separated from the reaction mixture. It boiled at $62-63^\circ$ at 20 mm. Bromination of this ether in chloroform gave a dibromide with a b.p. of $114-115^\circ$ at 10 mm.

Analysis of dibromide

0.1694 g substance: 0.2187 g AgBr.

Found %: Br 54.94.

$\text{C}_7\text{H}_{14}\text{O}_2\text{Br}_2$. Calculated %: Br 55.11.

The bromination of 2 g of the 1,4-chlorether in chloroform, using the theoretical quantity of bromine with cooling, gave 2.7 g of 1-chlor-2,3-dibrom-4-methoxybutane (yield 75%), with constants given in Table 4. It must be noted that the substance consists of a mixture of several stereoisomers, of which at least one is solid at ordinary temperatures: upon distillation of the dibromide, the last drops of distillate crystallize.

Analysis of dibromide

0.2045 g substance: 0.3771 g AgCl + 2AgBr.

Found %: Cl + 2 Br 69.43.

$\text{C}_5\text{H}_9\text{OClBr}_2$. Calculated %: Cl + 2 Br 69.64.

b) Into 100 ml of methyl alcohol, using mechanical stirring and a temperature of 40 to 42° , gaseous divinyl (67 ml) was passed, and 63 g of benzosulfodichloramide was added in small portions. The amount of dichloramide added was approximately equivalent to the amount of divinyl which had been passed through and practically completely dissolved. The temperature was sustained by the heat of the reaction. After 2.5 hours, the process of adding the dichloramide was complete: stirring was continued for about three hours more. Then a small quantity of sulfite was added to the solution, and it was subjected to distillation

with steam, as previously indicated. There was obtained in all 26 g of oil, which upon fractional distillation gave the following fractions:

1) to 120° - 1.4 g; 2) 120-130° 13.0 g (1,2-chlorether); 3) 130-140° - 1.3 g; 4) 140-150° - 0.8 g; 5) 150-160° - 5.5 g (1,4-chlorether); 6) 160-170° - 0.9 g; and 7) residue 0.5 g.

The total yield of monochlorethers was about 21 g, 35% of theory. Relative proportions of isomeric chlorethers: 1,2-chlorether - 70%, 1,4-chlorether - 30%.

The fraction from 120 to 130° had the following constants:

d_4^{20} 1.0262; n_D^{20} 1.4352.

0.1400 g substance: 0.1691 g AgCl.

Found %: Cl 29.88.

C_5H_9OCl . Calculated %: Cl 29.40.

The fraction with boiling range 150 to 160° had the constants:

d_4^{20} 1.0408; n_D^{20} 1.4548.

0.1311 g substance: 0.1604 g AgCl.

Found %: Cl 31.40.

C_5H_9OCl . Calculated %: Cl 29.40.

The data of analysis indicate that both fractions were somewhat contaminated with divinyl dichlorides.

2. Action of iodine and mercuric oxide upon a solution of divinyl in methyl alcohol. a) To a solution of 10 ml of divinyl (0.11 moles) in 25 ml of methyl alcohol were added 15 g of mercuric oxide, and then, with stirring and cooling to minus 15-10°, powdered iodine (25 g, 0.1 mole) in small portions, at a rate such that the temperature did not rise above minus 10°. After solution of all the iodine, the precipitate of mercurous iodide was filtered off and washed with alcohol. The iodoether which settled out when water was added to the solution was separated, washed with water, dried over $CaCl_2$, and distilled in vacuum. There was thus obtained 12.5 g of a material with constant boiling point, given in Table 1, 0.9 g of a fraction with boiling range 65 to 70°, which might be considered the same iodoether, and 0.7 g of a residue not less than half of which consisted of crystallized mercury compounds.

Analysis of 1,2-iodoether:

0.1535 g substance: 0.1699 g AgI.

Found %: I 59.83.

C_5H_9OI . Calculated %: I 59.86.

Thus, no significant quantities of the 1,4 product were observed in this experiment.

b) Into 53 g of mercuric oxide suspended in methyl alcohol (100 ml), gaseous divinyl was passed with mechanical stirring at a temperature from 35 to 40°, (the amount corresponded to 60 ml liquid divinyl), and at the same time, small portions of powdered iodine (127 g) were added. The amount of iodine added was sufficient to react with the divinyl passed in (and absorbed). When the reaction was complete, the mixture was treated in the usual way.

Upon distillation of the reaction product in vacuum at 20 mm, the following fractions were obtained: 1) 64-65° - 68 g (mostly at 64.5°; 1,2-iodoether); 2) 65-70° - 7.0 g; and 3) undistilled residue - 6 g (containing large quantities of mercury compounds).

Analysis of 1,2-iodoether:

0.1532 g substance: 0.1700 g AgI.

Found %: I 59.84

C_5H_9OI . Calculated %: I 59.86.

Analysis of the fraction boiling from 65 to 70° at 20 mm showed that it consisted of an admixture with diiodide or iodohydride of divinyl.

0.1767 g substance: 0.1965 g AgI.

Found %: I 60.11.

C_6H_9OI . Calculated %: I 59.86.

Upon heating 53 g of iodoether (fraction from 64 to 70°) with 35 g of KOH in 150 ml of ethyl alcohol for 30 minutes, there was obtained, after the usual treatment of the mixture, 15.5 g of methoxyprene with b.p. 74.5-75° and n_D^{20} 1.4460. Yield 74%. The residue after distillation of the methoxyprene weighed 0.3 g and had an odor characteristic for glycol ethers.

Upon heating the residue from the distillation of the iodoether (fraction 3) with alcoholic alkali, no diether of erythroglycol was obtained.

B. Addition of Ethylhypohalogenites

1. The reaction of divinyl with benzosulfodichloramide in ethyl alcohol.

a) To a solution of 135 ml of divinyl (1.5 moles) in 2.90 ml of ethyl alcohol (5 mole) at minus 12-8°, with mechanical stirring, 125 g of benzosulfodichloramide (0.5 mole) was added in small portions over a period of 3 hours. Stirring was continued for 3 hours at the same temperature. Then the precipitate of the addition product of the dichloramide with divinyl (containing active chlorine) was filtered off (17 g; 12% of theory; m.p. 58°), and the solution was treated as indicated in section A, 1a. A total of 34 g of chlorethers was obtained.

From the residue in a distillation flask (after steam-distilling off the chlorethers) there was separated out by means of a hot water extraction 36 g of benzosulfamide, a large quantity of addition products of the chloramide and divinyl (without active chlorine) being left behind.

Upon distillation of the chlorethers, at first at ordinary pressure and then in vacuum, the following fractions were obtained:

1) Up to 135° - 0.6 g; 2) 135-140° - 27 g (1,2-chlorether); 3) up to 60° at 15 mm - 1.2 g; 4) 60-70° - 1.8 g (1,4-chlorether); 5) 70-80° - 0.5 g; and 6) residue - 2.0 g.

Thus, the yield of monochlorethers totaled about 30 g, 22.4%. The ratio of isomeric chlorethers was: 1,2-chlorether - 95%; 1,4-chlorether - 5%.

Analysis of the fraction 135-140°:

0.1436 g substance: 0.1549 g AgCl.

Found %: Cl 26.68.

$C_6H_{11}OCl$. Calculated %: Cl 26.35.

From the 135-140° fraction, repeated distillation gave pure 1-chlor-2-ethoxy-butene 3, with constants given in Table 1.

0.1457 g substance: 0.1537 g AgCl.

Found %: Cl 26.09.

$C_6H_{11}OCl$. Calculated %: Cl 26.35.

Bromination of the 1,2-chlorether in chloroform gave the earlier described 1-chlor-3,4-dibrom-2-ethoxybutane with constants given in Table 4.

The greater part of the 60-70° fraction at 15 mm (1,4-chlorether) boiled from 62 to 64°. For this part, there was found:

0.1621 g substance: 0.1718 g AgCl.

Found %: Cl 26.22.

$C_6H_{11}OCl$. Calculated % Cl 26.35.

Upon treatment of the 60-70° fraction (15 mm) with an excess of a solution of KOH in ethyl alcohol, there was obtained the diethyl ether of erythroglycol, with b.p. 70.5 at 20 mm, and n_D^{20} 1.4256.

Upon heating 4.0 g of 1,4-chlorether (fraction 62-64° at 15 mm) with a solution of 3.5 g of KOH in 10 ml of methyl alcohol, there was obtained 2.7 g of the methyl ethyl ether of erythroglycol, (yield 69.8%) with a b.p. 62-62.5° at 20 mm.

Bromination of the 1,4 chlorether in chloroform gave 1-chlor-2,3-dibrom-4-ethoxybutane with constants given in Table 4. Yield totaled 85%.

Analysis of the dibromide:

0.1949 g substance: 0.3414 g AgCl + 2 AgBr.

Found %: Cl + 2 Br 65.92.

$C_6H_{11}OClBr_2$ Calculated %: Cl + 2 Br 66.33.

b) Upon carrying out the experiment with half quantities of the reagents under the same conditions, but in such a way that the entire process was completed in 2 hours, the yield of the addition product of the dichloramide with divinyl (containing active chlorine) amounted to 46 g (65% of theory), the yield of chlorethers 4.7 g (7%). The residue after distillation of the 1,2 chlor-ether weighed 0.4 g. From the residue in the distillation flask after the steam distillation of the chlorethers there was extracted with water a total of 5 g of amide.

c) Into 145 ml of ethyl alcohol, with mechanical stirring at a temperature of 35 to 40°, gaseous divinyl was passed (in all, 67 ml of liquid) and the dichloramide (62.5 g) added in small portions, as indicated in section A, 1b. At the end of the reaction, 100 ml of alcohol was distilled off from the reaction mixture on the water bath, and the residue steam distilled. After distillation of the alcohol, the solution contained no active chlorine. From the residue 25 g of amide and 23 g of products of the addition of chloramide with divinyl, without active chlorine, were obtained. Steam distillation gave 36.5 g of chlorethers. Upon fractional distillation of the material, the following fractions were separated:

1) Up to 135° - 1.4 g; 2) 135-140° - 22.2 g (1,2-chlorether) and further at 15 mm; 3) up to 60° - 1.8 g; 4) 60-70° - 5.4 g (1,4-chlorether); 5) 70-80° - 0.6 g; and 6) residue 1.1 g.

The yield of monochlorethers totaled 30.4 g, 45.2%. The ratio of isomeric chlorethers: 1,2-chlorether - 80%, 1,4-chlorether - 20%. For the 60-70° fraction, found d_4^{20} 1.0120; n_D^{20} 1.4522.

0.1876 g substance: 0.2135 g AgCl.

Found %: Cl 28.12.

$C_6H_{11}OCl$. Calculated %: Cl 26.35.

2. The reaction of divinyl with tertiary butylhypochlorite in ethyl alcohol.

To a solution of 80 ml of divinyl (a twofold excess) in 300 ml of ethyl alcohol at -12°, there was added over a period of 5 hours, with mechanical stirring, 45 g of

tertiary butylhypochlorite. As the reaction at first took place very sluggishly, 0.5 g of toluene sulfonic acid was added, and the solution during the following hour was illuminated with a mercury arc lamp, after which it contained only traces of active chlorine. The mixture was further treated in the usual manner. A total of 29 g of chloreters was obtained. Upon distillation, the following fractions were obtained:

1) Up to 135° - 0.5 g; 2) 135-140° 15.5g (1,2-chlorether); 3) 140-160° - 1.5 g and further at 15 mm; 4) up to 60° - 1.0 g; 5) 60-70° - 2.2 g (1,4-chlorether); 6) 70-100° - 0.9 g; and 7) residue - 4.0 g.

Thus, the yield of monochloreters amounted to about 22.5 g, 33%. The ratio of chlorether isomers: 1,2-chlorether - 88%, 1,4-chlorether - 12%. For the fraction from 60 to 70° at 15 mm, there was found: d_4^{20} 0.9987; n_D^{20} 1.4532.

3. The reaction of divinyl with chlorine and alcoholate in ethyl alcohol.

To a solution of 31 g of metallic sodium in 500 ml of ethyl alcohol, which had been cooled to minus 5°, 135 ml of divinyl was added, and then, to the mixture obtained, 71 g of gaseous chlorine was passed in with mechanical stirring at a temperature of -6 to 7°. (The chlorine was obtained from a calculated quantity of potassium permanganate). At the end of the reaction, 5.2 g of chlorine was found to be present in the solution bound to sodium hydroxide, and 42.2 g in the form of chlorine ion. The mixture was then treated in the usual fashion. The results of the fractional distillation of the reaction products:

1) Up to 130° - 2.5 g; 2) 130-140° - 13.6 g; 3) 140-160° - 1.6 g, and further at 15 mm; 4) up to 60° - 1.6 g; 5) 60-70° - 4.2 g; 6) 70-80° - 1.6 g; 7) 80-100° - 4.0 g; and 8) residue - 19.5 g.

Found for fraction from 135° to 140°:

0.1248 g substance: 0.1743 g AgCl.

Found %: Cl 34.55.

$C_8H_{11}OCl$. Calculated %: Cl 26.35.

$C_4H_8Cl_2$. Calculated %: Cl 56.75.

The data of analysis here given indicate that this fraction contained about 73% of the chlorether and 27% of the dichloride.

For the fraction boiling at 60-70° at 15 mm, found: d_4^{20} 1.0752, n_D^{20} 1.4592.

0.1495 g substance: 0.2146 g AgCl.

Found %: Cl 35.58.

$C_8H_{11}OCl$. Calculated %: Cl 26.35.

$C_4H_8Cl_2$. Calculated %: Cl 56.75.

The data of analysis indicate that the material contained 70% of the chlorether and 30% of the dichloride.

Thus the yield of monochlorether in this experiment consisted of 16 g, 12%. The ratio of the isomeric chloreters: 1,2-chlorether - 75%; 1,4-chlorether - 25%.

In order to determine whether it was possible for the 1,4-dichloride of divinyl (1,4-dichlorbutene-2) to be transformed in the process of this reaction into the 1,4-chlorether, the following experiment was set up. To a solution of 1.8 g of metallic sodium in 35 ml of absolute ethyl alcohol, 10 g of 1,4-dichlorbutene-2 was added. After standing for a day, the sodium chloride was filtered off, washed with alcohol, and dried. The yield was 4.2 g, 91%. The oil which separated out upon dilution of the filtrate with water was removed, washed with water, and dried over $CaCl_2$ and distilled. Yield, 4 g.

B.p. 60-65° at 15 mm; d_4^{20} 0.9998; n_D^{20} 1.4542.

0.1349 g substance: 0.1541 g AgCl.

Found %: Cl 28.19.

$C_8H_{11}OCl$. Calculated %: Cl 26.35.

4. The reaction of divinyl with benzosulfodibromamide in ethyl alcohol.

a) To a solution of 60 ml divinyl in 175 ml of ethyl alcohol at -10-8°, 80 g of benzosulfodibromamide was added in the course of 3 hours with mechanical stirring. After removing the active bromine (traces) with sodium bisulfite, the bromether was steam distilled along with the alcohol. After dilution of the distillate with water, 46 g of oil was obtained (after washing with water and drying over $CaCl_2$). From the residue, 36.5 g of sulfamide was separated (90%), as well as 2.5 g of the addition product of bromamide and divinyl.

Results of the distillation of bromether at 20 mm:

1) 56-56.5° - 4.2 g (1,2-bromether); 2) 56.5-60° - 0.6 g; 3) 60-132° - 0.6 g; 4) 132-134° - 0.8 g (dibromdiethoxybutane); and 5) residue 0.3 g.

Thus, the yield of monobromether was about 43 g, 48%. No 1,4-bromether was observed.

For the 60-132° fraction, there were found:

0.1704 g substance: 0.1665 g AgBr

found %: Br 41.58.

$C_8H_{11}OBr$. Calculated %: Br 44.65.

Found for the 132-134° fraction: d_4^{20} 1.5200, n_D^{20} 1.4942. MR_D 58.24.

$C_8H_{16}O_2Br_2$. Calculated MR_D : 57.96.

0.1533 g substance : 0.1919 g AgBr.

Found %: Br 53.27

$C_8H_{16}O_2Br_2$. Calculated %: Br 52.57.

b) Upon conducting the same reaction at 40-45° under the conditions described in A 1-b (70 g of dibromamide was taken for the reaction), 42 g of dibromether was obtained.

Results of distillation at 20 mm:

1) 56-56.5° - 38 g; 2) 56.5-60° - 0.5 g; 3) 60-132° - 0.6 g; 4) 132-134° - 1.4 g; and 5) residue 0.2 g.

Thus, the yield of 1,2-bromether in this experiment was about 39 g, 50%. No 1,4-bromether was found. It might have been present in quantities smaller than 2%.

5. The reaction of divinyl with iodine and mercuric oxide in ethyl alcohol.

a) To a solution of 135 g of divinyl in 300 ml of ethyl alcohol, 154 g of freshly precipitated mercuric oxide was added, and then, with mechanical stirring and cooling (-12 to 8°) small portions of 254 g of iodine were added. After separation of the precipitate of mercurous iodide, the solution was treated in the usual fashion.

Results of the fractional distillation of the reaction product (158 g) at 7 mm:

1) 54-54.5° (chiefly at 54.25°) 141.7 g (1,2-iodoether); 2) 54.5-60° - 7.0 g; 3) residue 8.5 g. Yield of 1,2-iodoether 66%.

The constants of the fraction from 54 to 54.5° are given in Table 1.

0.1770 g substance: 0.1850 g AgI.

Found %: I 56.50.

$C_8H_{11}OI$. Calculated %: I 56.15.

Found for the residue:

0.1752 g substance: 0.2051 g AgI.

Found %: I 63.28.

$C_8H_{11}OI$. Calculated %: I 56.15.

$C_8H_{16}O_2I_2$. Calculated %: I 63.79.

The 1,2-iodoether which had been treated with an alcoholic solution of KOH under the usual conditions gave a 70% yield of ethoxyprene with constants: b.p. 93-93.5°; d_4^{20} 0.8168; n_D^{20} 1.4420. Found previously for ethoxyprene: b.p. 93-94°; d_4^{20} 0.8177; n_D^{20} 1.4430.

Treatment of the residue with an alcoholic solution of KOH gave a product sharply differentiated in its properties from the diethyl ether of erythroglycol with n_D^{20} 1.4450, and with an extended boiling range. After agitation of this product with 5% H_2SO_4 , the solution gave a test for diacetyl with hydroxylamine and $NiSO_4$.

b) As a result of the action of iodine and mercuric oxide upon the solution of divinyl in ethyl alcohol at 40-45° under the conditions described in section A 2-b, there were obtained results that differed little from those obtained in the previous section.

C. The Addition of Butylhypochlorite.

1) The reaction of divinyl with benzosulfodichloramide in butyl alcohol.

a) Under the usual conditions, the action of 63 g of the dichloramide upon a solution of 65 ml of divinyl in 185 g of n-butyl alcohol at -15-10° gave 42.1 g (60% of theory) of the addition product of divinyl and the dichloramide containing active chlorine, and only 5.7 g of a mixture of the chlorethers. The reaction was carried out in the course of 6 hours.

Results of the fractional distillation of the chlorethers at 20 mm:

1) Up to 75° - 0.5 g; 2) 75-85° - 3.6 g (1,2-chlorether); 3) 85-95° - 0.4 g; 4) 95-105° - 0.9 g (1,4-chlorether); and 5) residue - 0.2 g.

Thus the yield of monochlorethers in this experiment amounted to 5.2 g, 6.4%.

From the 75-85° fraction, as the result of several redistillations, there was separated a fairly pure 1,2-chlorether with constants given in Table 1.

0.1730 g substance: 0.1534 g AgCl.

Found %: Cl 21.94.

$C_8H_{15}OCl$. Calculated %: Cl 21.80.

The 95-105° fraction did not represent a pure compound, as it contained less chlorine than was required for the 1,4-chlorether.

0.1703 g substance: 0.1356 g AgCl.

Found %: Cl 19.61.

$C_8H_{15}OCl$. Calculated %: Cl 21.80.

b). The action of dichloramide (65 g) upon a solution of divinyl (67 ml) in 185 g of butyl alcohol at 40-45° gave 17 g of a mixture of chlorethers.

Results of fractional distillation at 20 mm:

1) Up to 75° - 0.8 g; 2) 75-85° - 9.9 g (1,2-chlorether); 3) 85-95° - 0.9 g; 4) 95-105° - 2.5 g (1,4-chlorether); and 5) residue - 0.3 g.

Thus the yield of monochlorethers amounted to about 13.8 g, 17%. The ratio of isomers of the chlorethers: 1,2-chlorether - 82%, 1,4-chlorether - 18%.

The greater part of the second fraction, after repeated distillation, boiled at 76.5-77.5° at 20 mm. The constants of this part are given in Table 1.

0.1508 g substance: 0.1335 g AgCl.

Found %: Cl 21.90.

$C_8H_{15}OCl$. Calculated %: Cl 21.80.

The greater part of the fourth fraction boiled at 95-100° at 20 mm (2 g). Found for this part: d_4^{20} 0.9544, n_D^{20} 1.4498.

0.1403 g substance: 0.1169 g AgCl.

Found %: Cl 20.61.

$C_8H_{15}OCl$. Calculated %: Cl 21.80.

Upon redistillation of the 75-80° fraction at ordinary pressure over powdered KOH, a small yield of butoxyrene was obtained. B.p. 65-67° at 54 mm and n_D^{20} 1.4445. Previously found for butoxyrene: B.p. 65° at 54 mm, n_D^{20} 1.4450.

Heating 4 g of the 95-100° (at 20 mm) fraction with a solution of 3.5 g of KOH in n-butyl alcohol gave 2.7 g (yield 55%) of the dibutyl ether of erythroglycol with b.p. 129-132° at 20 mm and n_D^{20} 1.4365. For purposes of comparison the same ether was obtained by the action of a solution of KOH in n-butyl alcohol upon 1,4-dibrombutene-2 (10 g). The yield amounted to 4.3 g, b.p. 131-132° at 20 mm, n_D^{20} 1.4450.

The action of a solution of bromine in chloroform on the dibutyl ethers of erythroglycol obtained by different methods gave one and the same dibromide with constants shown in Table 4.

Analysis of the dibromide:

0.1815 g substance: 0.1906 g AgBr.

Found %: Br 44.69.

$C_{12}H_{24}O_2Br_2$. Calculated %: Br 44.38.

The bromination of the 1,2-chlorether in chloroform with the calculated quantity of bromine gave a dibromide with constants given in Table 4. Yield, 88%.

0.1668 g substance: 0.2685 g AgCl + 2AgBr.

Found %: Cl + 2Br 60.46.

$C_8H_{15}OClBr_2$. Calculated %: Cl + 2Br 60.55.

SUMMARY

1. An investigation has been made of the influence upon the order of addition of alkylhypohalites to divinyl of: the nature of the halogen, the size of the alkyl radical, the temperature, the duration of the reaction, the method of hypohalogenation.

2. It has been determined that the addition of alkylhypochlorites to divinyl always gives a mixture of 1,2- and 1,4-chlorethers, with a great predominance of the former. At the same time, the addition of alkylhypobromites and alkylhypoiodites in the temperature range from -12° to +45° apparently takes place with the formation of the 1,2-halogen ether alone.

3. It has been shown that with the increase in size of the alkyl radical, the relative yield of 1,4-chlorether decreases, along with a sharp decrease of

the total yield of chlorethers. On the other hand, at a higher temperature, the relative yield of the 1,4-chlorether increases and the total yield of chlorethers increases.

4. With a decrease in the time of carrying out the reaction at low temperatures, there is a sharp increase in the yield of the addition product of divinyl and the dichloramide, and the yield of chlorethers diminishes. On the basis of this observation, the conclusion has been reached that the reaction of the dichloramide with alcoholic solutions of divinyl takes place in two steps: first the dichloramide adds to the divinyl, then the product containing active chlorine which has been formed reacts with the alcohol and divinyl to form chlorethers. However, this mechanism is not the only one: with a rise in temperature, a growing role is played by the process of direct reaction of the dichloramide with the alcoholic solutions of divinyl to form chlorethers and amide.

5. It has been determined that different methods of carrying out the addition reaction of alkylhypochlorites to divinyl give different relative yields of the isomeric chlorethers, although the yield of the 1,2-chlorether always greatly predominates.

6. The specific behavior of hypohalite compounds in addition reactions with conjugated systems can be explained on the basis of contemporary electron theory.

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Received March 26, 1948.

THE BROMINATION AND INTRODUCTION OF THE IODOXY GROUP INTO NEW DIENE HYDROCARBONS WITH CONJUGATED SYSTEMS OF DOUBLE BONDS. VII.

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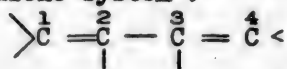
In the development of our work [1] on the introduction of halogen into aliphatic olefin and diene hydrocarbons with conjugated systems of double bonds, it became necessary to broaden the range of investigation, including within it diene hydrocarbons with a new structure of the carbon skeleton, among them ω -methylene groups, and to trace their behavior in reactions that involve bromination and introduction of the iodoxy group.

One of the simplest representatives of the dienes with ω -methylene groups, isoprene [2], is brominated under the conditions of the MacIlliny method in such a manner that its iodine number amounts to approximately half of its theoretical value, and despite the presence in isoprene of a quaternary C atom at the double bond, the separation of a small quantity of HBr is observed.

The bromination of diisopropenyl (Table 1) with different amounts of excess bromine present in the reaction mixture showed also that approximately a single molecule of bromine was consumed in the reaction, and despite the presence of as many as two quaternary atoms, the quantity of bromine splitting off in the form of HBr is small and amounts to 3.3 to 4.3% of the total consumption of bromine in the reaction. Thus isoprene and diisopropenyl are examples of exceptions to the rule of M.D.Lvov and D.V.Tishchenko, by virtue of the formation in predominant amounts of the 1,4-dibromides.

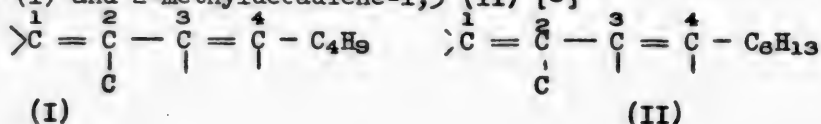
For lack of factual data, it remains an open question to what extent the high degree of conjugation of the double bonds is preserved, as manifested in a tendency to form 1,4-dibromides, when heavier radicals are present in the 2,3-positions, or when the diene molecule is deprived of symmetry.

Another influence on the degree of conjugation of the bonds is shown by the introduction into the diene system:



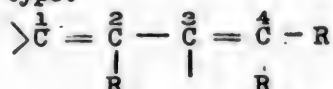
of radicals in the 2 and 4 positions. Thus, 2,6-dimethylheptadiene-1,3 [1], upon the introduction of 50% of the amount of bromine required by theory, splits off bromine in the form of HBr to the amount of 8.6% of the total consumption of bromine in the reaction; this is considerably higher than with diisopropenyl, and shows that the 1,2 double bond (I), thanks to the disturbance of the conjugation, reacts with great ease.

It is important to note that with identical radicals on the 2 carbon, the degree of conjugation is the more strongly disturbed the greater the mass of the radical attached to carbon 4. This can be seen from the comparative data on the bromination of (I) and 2-methyldecadiene-1,3 (II) [3]



Upon the introduction into the reaction of a quantity of bromine sufficient for the saturation of both double bonds, the iodine number of (II) reaches 80%, and that of (I) 70%, of the theoretical value; in addition, (II) splits off bromine as HBr to the extent of 13.8%, (I) 10.6%; this testifies to a greater degree of independence of the 1,2 double bond in 2-methyl-decadiene-1,3.

A still greater disturbance of the conjugation of the double bonds is observed with dienes of the type:

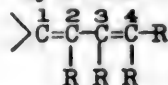


The independence of the double bonds increases, while with regard to bromine, the 3,4 double bond becomes more active than the 1,2 bond, as can be seen from the example of 2,4-dimethylpentadiene-1,3 (III) and especially in the case of 2-tertiary butyl-4,5,5-trimethylhexadiene-1,3 (IV).



If the addition of bromine to (IV) took place at the 1,2 bond, the splitting off of HBr would either not take place at all, or would take place only to a negligible extent. Actually, upon the introduction of a quantity of bromine sufficient for the saturation of one double bond, (IV) splits off 17.9% of bromine in the form of HBr; this can be understood only if bromination took place at the 3,4 double bond.

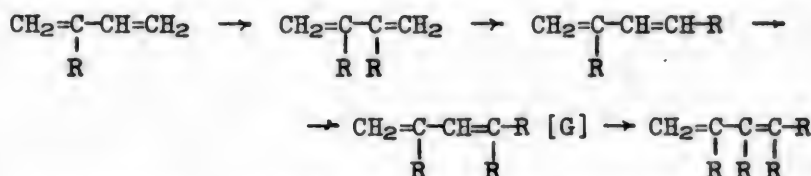
Further, with diene hydrocarbons of the type:



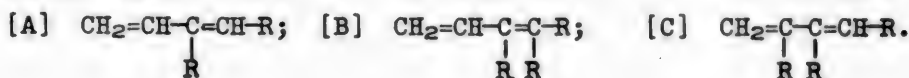
thanks to the additional shielding effect of the radical at carbon 3, the degree of conjugation of the bonds becomes still less; this is obvious from a comparison of the data for (III) with those for the specially synthesized 2,3,4-trimethylhexadiene-1,3 (V) [4].

The splitting off of HBr from (V), no matter how much bromine is introduced into the reaction, is greater than in the case of (III); in addition (V) also is comparatively more receptive to bromine, a fact which is explained by the greater independence of the double bonds in (V).

Taking as a basis the destruction of the degree of conjugation of the ethylene bonds, the diene hydrocarbons we have considered may be arranged in the series:



Consequently, of the given group of diene hydrocarbons, three types remain to be considered;



We must suppose that diene [B] will have a greater degree of conjugation than diene [C], because in its molecule all three radicals are attached to a single double bond.

A comparison of the properties of the series of diene hydrocarbons under consideration permits the formulation of the rule: "With an increase in the number of quaternary carbon atoms, comprising the skeleton of the conjugated system, the degree of conjugation of the ethylene bonds decreases, or, what amount to the same thing, the independence of the ethylene bonds increases."

In addition, the degree of conjugation of the ethylene bonds depends also upon the position of the radicals inside the system, and therefore, "With an equal number of identically constituted radicals present and attached to the carbons of the conjugated system, their influence upon the degree of conjugation is greater, the less symmetrical their position in the system!"

These empirical rules are confirmed by the data on the bromination of diene hydrocarbons derived from 1,4-dialkylated butadiene-1,3. The simplest representative of this series of hydrocarbons, hexadiene-2,4, thanks to the high degree of conjugation of the double bonds, is brominated to the point of saturation of half the double bonds; this testifies to the formation of the 1,4-dibromide [3]. Consequently, upon the introduction of CH_3 - or C_2H_5 - at carbon 2 of the conjugated system, there is observed an increased receptivity of such hydrocarbons to bromine, and along with it, a separation of bromine in the form of HBr which reaches 5 to 7% even at 50% of the bromine norm. As an example, we may take 3-methyl-octadiene-2,3 (VI) and 3-ethyl-octadiene-2,4 [4], both of which, as a result of the weakening of the conjugation, show an increased independence of the double bonds formed by quaternary carbons. In this series too, along with an increase in the mass of the radical upon carbon 4, the independence of the 1,2 double bond increases, as is obvious from a comparison of the data for (VI) and 2,6-dimethyl octadiene-4,6 (VII). The latter diene, obtained by us in much purer condition than by Abelman [5], splits off more bromine in the form of HBr than does (VI):



The introduction of a fourth radical into the conjugated system, especially at carbon 4, produces a still greater lowering of the degree of conjugation of the double bonds, as is evident from the example of 2,4-dimethylhexadiene-2,4 (VIII) [4], and also from 3-methyl-5-ethylheptadiene-3,5 [4], both of which split off still greater amounts of bromine in the form of HBr , especially at 100% of the bromine norm.

The introduction of a fifth radical at carbon 3 of the conjugated system increases the number of quaternary carbon atoms within it, and leads to a still greater increase in the independence of the double bonds; as an example, there is the synthesized 3,4,5-trimethylheptadiene-2,4, which splits off more HBr upon bromination than does (VIII).

Thus, these diene hydrocarbons may also be arranged in a series according to the destruction of the amount of conjugation of the double bonds:

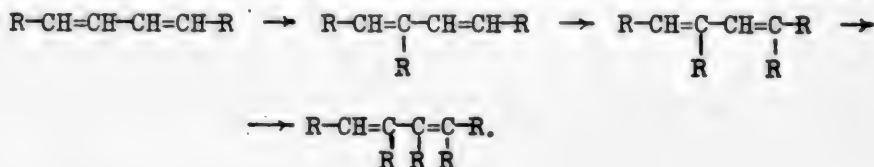


Table 1
The bromination of diene hydrocarbons

No. of expts.	weight (gm)	amount of Br-CCl ₄ solution (ml)	Amount of 0.1 N Na ₂ S ₂ O ₃ solution (ml)			Total iodine number	iodine number of material split off	Genuine iodine no.	percent of halogen transformed into HBr, of total halogen consumed
			used to titrate excess of halogen	Equiv. to I consumed by weight	used in titrating iodine from HI				
2,6-dimethylheptadiene-1,3							theory 409.02		
1	0.1489	3.58	—	15.75	1.33	134.80	15.76	119.04	8.44
2	0.0704	3.86	2.11	13.16	1.40	237.14	50.48	186.66	10.63
2,4-Dimethylpentadiene-1,3							theory 528.34		
1	0.1452	6.76	0.22	30.40	3.83	265.74	58.21	207.53	10.95
2	0.1075	9.92	10.84	34.10	5.82	402.63	137.43	265.20	17.07
2-Tert-butyl-4,5,5-trimethylhexadiene-1,3							theory - 281.76		
1	0.1474	3.70	0.10	16.10	2.87	138.64	49.43	89.21	17.82
2	0.1046	5.35	2.33	21.09	4.89	255.92	118.67	137.25	23.18
2,6-Dimethyloctadiene-4,6 with b.p. 168.5°-170.5°							theory - 367.52		
1	0.1596	4.75	0.02	17.16	1.78	136.47	28.31	108.15	10.37
2	0.0938	5.58	2.83	17.35	2.67	234.78	72.26	162.52	15.38
3,4,5-Trimethylheptadiene-2,4 with b.p. 157-159°							theory - 367.52		
1	0.1692	7.67	0.27	24.41	3.85	183.11	57.91	125.20	15.81
2	0.1216	11.36	2.60	33.96	9.93	354.38	207.30	147.08	29.24
2,3-Dimethylbutadiene-1,3 [a]							theory 618.56		
1	0.0557	3.73	0.35	13.22	0.42	301.26	19.14	282.12	3.17
2	0.0240	3.25	5.72	6.10	0.26	322.61	27.50	295.11	4.26
2,3-Dimethylbutadiene-1,3 [b]									
1	0.0959	5.95	0.02	23.55	1.06	311.70	28.05	283.65	4.50
2	0.0795	9.90	18.86	20.36	0.95	325.07	30.33	294.74	4.66
3,5-Dimethylheptadiene-2,4 with 2-ethyl-4-methylhexadiene-1,3, with b.p. 139-144°									
1	0.0834	3.33	0.09	13.56	2.16	206.37	65.74	140.63	15.92
2	0.0476	3.90	2.42	13.61	4.05	362.92	215.99	146.93	29.75
4-Ethylnonadiene-3,5 or 3-propyloctadiene-2,4 with b.p. 166-168°.									
1	0.0756	10.0	25.66	11.39	1.50	191.23	50.36	140.87	13.16
2	0.0828	10.0	24.92	2.13	1.50	185.94	45.98	139.96	12.36

Finally, from a comparison of the behavior of (I) and (VII) upon bromination, relative to (III) and (VIII), it is clear that the entrance of CH₃- at carbon 1 of the conjugated system produces a decrease in the degree of conjugation of the double bond.

Everything said above indicates that the application of the bromination reaction to diene hydrocarbons with conjugated systems of double bonds may be utilized for analytical purposes. But what is especially important, it also permits us to reveal the relationship between the structure of their molecules and the degree of conjugation of the double bonds, which is reflected in the tendency of the diene hydrocarbons to react. The latter show the entire gamut of transitions from reaction as a system to reaction as separate, apparently independent double bonds, (Table 1).

In consequence of the highly characteristic properties of the bromides obtained at the 50% or 100% bromine norm, we are presenting data for the splitting off of HBr from the portions titrated (Table 2).

Table 2
Degree of splitting off of HBr from hydrocarbon bromides

Expt. No	Name of hydrocarbon	Quantity bromine used in bromination, expressed as % of amount needed for complete saturation of double bonds	Bromine split off as HBr as % of total bromine used up in reaction		
			during 30 min. expt.	Upon standing quietly	
				1 hour	2 hours
1	2,3-Dimethylbutadiene-1,3[a]	50	3.17	1.36	1.51
2	100	4.26	1.50	1.54
1	2,6-Dimethylheptadiene-1,3	50	8.44	2.49	4.71
2	100	10.63	1.70	2.97
1	2,4-Dimethylpentadiene-1,3	50	10.95	20.50	29.51
2	100	17.07	3.43	6.54
1	2-Tert. butyl-4,5,5-trimethylhexadiene-1,3	50	17.82	28.88	28.90
2	100	23.18	1.51	2.37
1	2,6-Dimethyloctadiene-4,6	50	10.37	5.39	7.73
2	100	15.38	0.54	0.95
1	3,4,5-Trimethylheptadiene-4,6	50	15.81	17.37	22.33
2	100	29.24	1.06	1.85

In the present work, we did not attempt to make a detailed investigation of the course of the reaction for introducing the iodoxy group, and limited ourselves merely to the selective determination of iodine numbers for individual diene hydrocarbons. The experimental results (Table 3) show that the introduction of the iodoxy group takes place more completely the lower the degree of conjugation of the double bonds, that is, they completely confirm the conclusions drawn from a study of the bromination reaction.

II

In the light of what has been said above, we can now explain the cause of the occasionally very impure course of the Diels-Alder reaction. In our series of communications on the synthesis of diene hydrocarbons, we have more than once stated that the reaction under investigation was accompanied by polymerization reactions of the dienes, and in our latest work [8] we indicated

Table 3

Introduction of the Iodoxy Group into Diene Hydrocarbons.

Expt. No.	Weight in g of sample	Amount 0.1N Na ₂ S ₂ O ₃ solution (ml)			Iodine No.	Iodine changed to HI (in %)	
		Used to titrate excess iodine	Corresponding to iodine used up for sample	Used to titrate iodine from HI			
	2,3-Dimethylbutadiene-1,3 [a]						
1	0.0812	71.60	20.62	16.96	322.32	82.25	
2	0.0521	76.71	15.51	12.03	377.86	77.56	
	2,4-Dimethylpentadiene-1,3						
1	0.0878	61.20	27.76	21.41	401.31	77.12	
2	0.0846	60.80	28.16	19.60	422.48	69.60	
	2-Tert. butyl-4,5,5-trimethylhexadiene-1,3						
1	0.2517	15.09	11.59	6.33	58.44	54.61	
2	0.2391	15.53	11.15	6.40	59.19	57.39	
	2,4,5-Trimethylheptadiene -2,4						
1	0.1623	27.37	18.00	15.84	140.77	88.00	
2	0.0636	68.40	28.63	25.40	571.38	88.71	
	2,3,4-Trimethylhexadiene-1,3						
1	0.0403	81.24	15.79	13.01	497.32	82.39	
2	0.0436	80.02	17.01	15.08	495.19	88.65	
	3,5-Dimethylheptadiene-2,4 with 2-ethyl-4-methylhexadiene-1,3						
1	0.0384	79.89	16.43	13.82	543.03	84.11	
2	0.0620	70.10	26.22	21.88	536.79	83.41	

that only when the dienes are practically free from the tendency to polymerize may we hope for a quantitative recovery of the adduct. Actually, only in the case when the speed of the Diels-Alder reaction is considerably greater than the speed of the polymerization reaction can we obtain the adducts in good yield.

But the basic cause, as it now appears to us, is not confined to this interlocking of the reactions, but includes once more the degree of conjugation of the double bonds. Those dienes which possess a high degree of conjugation of the double bonds easily give pure adducts, those dienes with a high degree of independence of the double bonds naturally enter more easily into other, side reactions. Consequently, the question is here not limited to the degree of polymerizing tendency of the diene; 2,3-dimethylbutadiene-1,3 polymerizes more easily than 3-methyl-5-ethyl-heptadiene-3,5, and at the same time forms an adduct in very good yields, whereas the latter gives very much lowered values of the diene numbers.

Only when the molecules of the diene hydrocarbon react as a system does the Diels-Alder reaction proceed cleanly and with high yields of the adducts. Hence there follows the conclusion that the Diels-Alder reaction cannot have a general application for all substances with so-called conjugated systems, in view of the fact that many of these, because of their structure, react as practically separated double bonds, and are therefore hardly to be distinguished from olefins and diolefins, with independent double bonds. The views here developed must also be confirmed by a study of other reactions of diene hydrocarbons with a conjugated system of double bonds.

EXPERIMENTAL

1. Synthesis of New Diene Hydrocarbons with Conjugated Systems of Double Bonds

The syntheses were conducted in round-bottomed flasks of 1-liter capacity, with four necks. The center neck served for the introduction of a mechanical stirrer, one of the lateral necks served for the introduction of a dropping funnel for an absolute ether (1:1) solution of the α,β -unsaturated ketone and a thermometer. In the third neck was placed a dropping funnel for the absolute ether solution of RMgHal and in the fourth neck a short ball condenser.

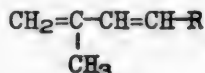
After introduction into the flask of 100 to 150 ml of absolute ether, previously cooled to -15° , the flask was placed in a cooling bath, where it was maintained all through the synthesis at a temperature from -12 to -17° . Then, after starting the mechanical stirring, the absolute ether solutions of the ketone and the RMgHal were dropped in through the dropping funnels in such a manner that there was no great excess of RMgHal at any moment. Usually, the dropping of the ketone solution was continued for 3 to 4 hours, the RMgHal solution for 6 hours. After the introduction of the ketone and the RMgHal, the flask with the reaction mixture continued to stand in ice overnight. The reaction products were decomposed with ice, and the subsequent addition of an NH_4Cl solution. The ether layer was separated, and the water layer salted out and extracted three times with ether. The ether solution was dried over Na_2SO_4 . After filtration of the Na_2SO_4 , the ether was distilled off on the water bath, and the residue subjected to dehydration by means of a double distillation with phthalic anhydride or anhydrous oxalic acid. The final purification of the diene hydrocarbons was accomplished by means of fractional distillations over metallic sodium in a current of dry CO_2 .

Synthesis of 2,6-dimethylheptadiene-1,3 : From every 12.6 g of isoamylideneacetone with b.p. $174-178^{\circ}$ at 748 mm, d_4^{20} 0.8470, n_D^{20} 1.4409, and CH_3MgI , prepared from 4.9 g of Mg, and 29 g CH_3I , in 40 ml of absolute ether, upon carrying out the synthesis in 100 ml of absolute ether, there was obtained about 15 g of reaction products, from which there was separated on an average 1.2 g of hydrocarbon with b.p. $143-144^{\circ}$ at 737 mm. The yield of hydrocarbon amounted to 9.5% of theory, d_4^{20} 0.7561; n_D^{20} 1.4520.

Found: MR_D 44.12.

$\text{C}_9\text{H}_{18}\text{F}_2$. Calculated: MR_D 42.83.

The bromination of this nonadiene (Table 1) took place as with the other dienes of the structure:



Synthesis of 3-methyloctadiene-2,4 : From 42.5 g freshly distilled butylidene acetone, with b.p. $165-167^{\circ}$ at 750 mm, d_4^{20} 0.8520, n_D^{20} 1.4424 and $\text{C}_2\text{H}_5\text{MgBr}$ prepared from 10.1 g of Mg and 45 g of $\text{C}_2\text{H}_5\text{Br}$ in 70 ml of absolute ether, upon carrying out the synthesis in 150 ml of absolute ether, there was obtained 44 g of reaction products; the greater part of this was high boiling substance with b.p. up to 195° at 300 mm, 23 g, and there also was a tarry residue of 9.5 g. From the alcoholic fraction with b.p. $170-171^{\circ}$ at 745 mm, 6.7 g was separated, or 12.4% of theory. d_4^{20} 0.8431; n_D^{20} 1.4392.

Found: MR_D 44.36.

$\text{C}_9\text{H}_{18}\text{O}$ F. Calculated: MR_D 44.82.

* With the aid of student I. A. Alekseyeva

** With the aid of student I. E. Titava

The true iodine number of 3-methyloctene-4-ol-3, found by MacIlleny's method, averaged 173.48, while the theoretical iodine number equaled 178.59.

The dehydration of alcohol was carried out by means of 2-distillations with anhydrous oxalic acid. A hydrocarbon was obtained with b.p. 152-153° at 737 mm; d_4^{20} 0.7723; n_D^{20} 1.4591.

The iodine number of the hydrocarbon by Hanus's method (2 hours) amounted on an average to 311.6 as compared to the theoretical 409.02, a typical result for diene hydrocarbons having three radicals in their skeleton at the 1,2 and 4 carbon atoms of the conjugated system.

The diene nature of the hydrocarbon is shown by the application of the Diels-Alder reaction. The adducts were transformed into acids, which were analysed in the form of their silver salts, dried to constant weight at 85°.

A. Ag salts from acids soluble in boiling water:

0.0407 g substance: 0.0192 g Ag.

0.0570 g substance: 0.0270 g Ag.

Found %: Ag 47.17, 47.36.

B. Ag salts from insoluble acids:

0.1050 g substance: 0.0372 g Ag.

Found %: Ag 35.42.

$C_{13}H_{18}O_4Ag_2$. Calculated %: Ag 47.53 (from monomer)

$C_{13}H_{18}O_4Ag_2$. Calculated %: Ag 37.32 (from dimer).

Because the dehydration of 3-methyloctene-4-ol-3 could give two isomeric hydrocarbons: 2-ethylheptadiene-1,3 and 3-methyloctadiene-2,4, the hydrocarbon with b.p. 152-153° was subjected to oxidation in order to determine its structure. To 1 g of the nonadiene and 10 g of ice, 6 g of finely powdered $KMnO_4$ in 50 ml water was added in three stages, the heat of the reaction being removed by cooling the reaction flask with snow. After standing overnight, all the $KMnO_4$ had been reduced. After making the solution alkaline with K_2CO_3 solution, the potassium salts were concentrated to a small volume and decomposed with dilute sulfuric acid. The organic acids were separated by the method of E.E.Vagner [7] in 4 fractions and analyzed in the form of Ag salts.

Analysis of Ag salts of acids from fraction 1:

0.0570 g substance: 0.0288 g Ag.

0.0646 g substance: 0.0366 g Ag.

Found %: Ag 56.47, 56.65.

$C_4H_7O_2Ag$. Calculated %: Ag 55.34.

Analysis of Ag salts of acids from fraction 4:

0.0614 g substance: 0.0397 g Ag.

0.0800 g substance: 0.0520 g Ag.

Found %: Ag 64.65, 65.00.

$C_2H_3O_2Ag$. Calculated %: Ag 64.63.

The formation during oxidation of a nonadiene fatty acid and acetic acid indicated its structure to be 3-methyloctadiene-2,4. Consequently, dehydration of 3-methyloctene-4-ol-3 took place with the H atom splitting off from the ethyl radical of the carbinol.

The synthesis of 2,6-dimethyloctadiene-4,6. In a control experiment, from 22 g isoamylidene acetone and the C_2H_5MgBr prepared from 8.5 g Mg and 42 g C_2H_5Br in 70 ml of absolute ether, there was obtained 23 g of reaction product. Upon fractional distillation (39 mm), the following fractions were obtained: 1) up to $100^\circ - 2.4$ g; 2) $100-102^\circ - 4.5$ g; 3) $102-105^\circ - 4.9$ g; 4) $105-170^\circ - 4.3$ g; and residue with b.p. above $170^\circ - 5.0$ g.

The second fraction, a transparent liquid with a pleasant, weak floral odor, was chiefly 2,6-dimethyloctene-4-ol-6.

d_4^{20} 0.8352; n_D^{20} 1.4325.

Found: MR_D 48.54.

$C_{10}H_{20}OF$. Calculated: MR_D 49.43.

Fractions 1, 2 and 3 were combined and dehydrated with anhydrous oxalic acid. There was obtained 5.2 g of hydrocarbon with b.p. $165-170^\circ$ at 745 mm. The yield amounted, on an average, to 21.5% of theory.

The wide range of boiling points of the hydrocarbon testified to the fact that the dehydration of the tertiary alcohol proceeded in two different directions, with the formation of isomeric hydrocarbons: 2-ethyl-6-methylheptadiene-1,3 and 2,6-dimethyloctadiene-4,6.

Abelmann [5] obtained 2,6-dimethyloctadiene-4,6 from tiglic aldehyde and isoamyl magnesium bromide; for this hydrocarbon: b.p. $164-167^\circ$; $d_4^{14.5}$ 0.7832; $n_D^{14.5}$ 1.4665.

In order to obtain more accurate data for the 2,6-dimethyloctadiene-4,6 obtained by us to the amount of 17.4 g, the hydrocarbon was subjected to repeated fractionation above Na in a stream of CO_2 at 736 mm. There were obtained: fraction 1, $160-162.5^\circ - 1.4$ g; fraction 2, $162.5-168.5^\circ - 7$ g; fraction 3, $168.5-170.5^\circ - 6.6$ g. The hydrocarbon with b.p. $160-162.6^\circ$ had d_4^{20} 0.7729; n_D^{20} 1.4526. Found MR_D 48.27; $C_{10}H_{18}$ 2. Calculated MR_D 47.44.

The hydrocarbon with b.p. $168.5-170.5$ had d_4^{20} 0.7741; n_D^{20} 1.4558.

Found: MR_D 48.49

$C_{10}H_{18}$ 2. Calculated: MR_D 47.44.

The diene nature of these hydrocarbons was shown by their bromination (Table 1). The hydrocarbon with b.p. $168.5-170.5^\circ$ was thus shown to be 2,6-dimethyloctadiene-4,6, mixed with a small quantity of its isomer. The inclusion of the latter was deduced from the results of oxidation of the hydrocarbon with b.p. $168.5-170.5^\circ$ by means of $KMnO_4$. The organic acids obtained were separated by the method of E.E.Vagner into 4 fractions. From the acids of fraction 1 there was obtained 0.1620 g of silver salts, with an average content of 53.1% Ag; from the acids of fraction 2, 0.20 g Ag salts, separated by crystallization into a more difficultly soluble Ag salt to the amount of 0.1120 g with a content of 59.15% silver, and a more easily water-soluble Ag salt to the amount of 0.0744 g with a content of 63.64% silver. From the acids of fractions 3 and 4, Ag salts were obtained in very small quantities. Upon concentration of their solutions, strong decomposition was observed, evidence of the presence of formic acid.

Thus, among the oxidation products of the hydrocarbon with b.p. $168.5-170.5^\circ$ were found: isovalerianic acid, acetic acid, and a very small quantity of formic acid.

In view of the relative yields of isomeric decadiene, we must suppose that in the dehydration of 2,6-dimethyloctene-4-ol-6 with the splitting off of the elements of water, a great role is again played by the ethyl radical, and a much smaller role by the methyl radical of the carbinol.

With the aid of students E. V. Gorbunova, Z. I. Tutinina, L. F. Goods, and A. Johansen.

The synthesis of 2,4-dimethylpentadiene-1,3.* In order to study the behavior upon bromination (Table 1) of diene hydrocarbons with a single radical upon the 2nd and two radicals upon the 4th carbon of the conjugated system, the synthesis of the hydrocarbon in question was undertaken by the methods that had been developed by us. From 16 g of mesityl oxide and the CH_3MgI obtained from 8 g of magnesium and 48 g CH_3I in 50 ml absolute ether, the synthesis being carried out in 100 ml of absolute ether at -10 -- -12° , there was obtained on an average 6 g of 2,4-dimethylpentadiene-1,3. The yield of diene amounted to 38.40% of theory. The hydrocarbon had b.p. 94° at 756 mm; d_4^{20} 0.7430; n_D^{20} 1.4413.

Found: MR_D 34.17.
 $\text{C}_7\text{H}_{12}\text{F}_2$. Calculated: MR_D 33.59.

The tertiary alcohol corresponding to the given hydrocarbon was obtained by Fellenberg [8] from mesityl oxide and CH_3MgI with a yield of 27.5% of theory. In view of the inevitable loss during its dehydration, the yield of diene hydrocarbon would have been still lower.

2,4-Dimethylpentadiene-1,3 was first obtained by Grignard [9], who did not mention the yield. The hydrocarbon was described as a liquid with b.p. 93 -- 95° at 750 mm. Waterman and Koch [10] described this hydrocarbon as a substance with b.p. 93.1 -- 93.2° ; d_4^{20} 0.7368; n_D^{20} 1.4412. Ya. M. Slobodin [11] described it as having a b.p. 91 -- 93° , d_4^{20} 0.7299, and n_D^{20} 1.4334; R. Ya. Levina [12] and coworkers obtained the hydrocarbon in a yield of about 30% of theory, and give the b.p. as 93 -- 94° (755), d_4^{20} 0.7376, n_D^{20} 1.4443.

Synthesis of 2-tert.-butyl-4,5,5-trimethylhexadiene-1,3.** The 2,2,5,6,6-pentamethylheptene-4-one-3 obtained by the self-condensation of pinacolone served as the starting material. B.p. was 202 -- 203° at 745 mm, d_4^{20} 0.8525, n_D^{20} 1.4461.

From 16 g of the ketone, and twice the theoretically necessary amount of CH_3MgI , there was obtained on an average 7.4 g of the diene hydrocarbon when the synthesis was carried out in 100 ml of absolute ether at -15° . The hydrocarbon had a b.p. of 184 -- 185° at 740 mm. d_4^{20} 0.7872; n_D^{20} 1.4431.

Found: MR_D 60.69.
 $\text{C}_{13}\text{H}_{24}\text{F}_2$. Calculated: MR_D 61.30.

Bromination of the tridecadiene proceeded as with the other dienes of the given type, but because of the action of the CH_3 and $\text{C}(\text{CH}_3)_3$ upon the 4th carbon of the conjugated system, the independence of the 3,4-double bond was increased, and the stability of the dibromide therefore approached the stability of the dibromides from the di- and triisobutylenes.

Synthesis of 2,3,4-trimethylhexadiene-1,3.* Starting with 12.5 g of 3,4-dimethylhexene-3-one-5 with b.p. 157 -- 158° at 746 mm, d_4^{20} 0.8585, n_D^{20} 1.4418, and twice the theoretically necessary amount of CH_3MgI , the synthesis was carried out in 150 ml of absolute ether at -15° . There was obtained on an average from 3.3 to 3.5 g of the diene hydrocarbon, or 32.9% of theory. The 2,3,4-trimethylhexadiene-1,3 had a b.p. of 134 -- 135° at 768 mm; d_4^{20} 0.7701; n_D^{20} 1.4425.

Found: MR_D 42.68.
 $\text{C}_9\text{H}_{18}\text{F}_2$. Calculated: MR_D 42.82.

The bromination of the hydrocarbon was studied [4], and showed the great independence of the 3,4 double bond protected by the influence of the methyl groups upon the 2 and 3 carbons of the conjugated system.

* With the aid of laboratory worker M. V. Bobrova

** With the aid of student G. N. Lisienkova

2. The Synthesis of Mixtures of Isomeric Diene Hydrocarbons with a Conjugated System of Double Bonds

In carrying out the objective of explaining the degree of conjugation of the $>C=C<$ and $C=O$ bonds in α,β -unsaturated ketones on the basis of the yields of diene hydrocarbons, the following syntheses were undertaken.

Synthesis from 3-methylheptene-3-one-5 and CH_3MgI . * Starting with 12.5 g of ketone with b.p. 164° at 766 mm and twice the theoretically necessary amount of CH_3MgI , and carrying out the synthesis in a solution of 150 ml of absolute ether at -15° , there was obtained 6 g of hydrocarbon with a boiling range from 139 to 144° at 749 mm. The yield of diene hydrocarbons amounted to 35.7% of theory. The mixture of 2-ethyl-4-methylhexadiene-1,3 and 3,5-dimethylheptadiene-2,4 had d_4^{20} 0.7728, n_D^{20} 1.4460.

Found: MR_D 42.83.
 C_8H_{16} Γ_2 . Calculated: MR_D 42.82.

Bromination of the hydrocarbon mixture (Table 1) confirmed the fact that it belonged to the diene hydrocarbons having at least three radicals upon the carbons of the conjugated system.

Synthesis from 3,4-dimethylhexene-3-one-5 and C_2H_5MgBr . * Starting with 12.5 g of the ketone with b.p. $156-158^\circ$ at 746 mm, and twice the theoretically necessary amount of C_2H_5MgBr , the synthesis was carried out in 150 ml of absolute ether at -5° . There was obtained an average yield of 16 g of reaction product. Upon fractional distillation in vacuum, 7.9 g of an alcoholic fraction with a pleasant, weakly floral odor was recovered. The yield of 3,4,5-trimethylheptene-4-ol-3 amounted to 50.6% of theory. B.p. $88-90^\circ$ at 17 mm; d_4^{20} 0.8693; n_D^{20} 1.4556.

Found: MR_D 48.79.
Calculated: MR_D 49.43.

This alcohol was much more difficult to dehydrate than the previous ones. After several distillations with "predgon" and phthallic anhydride and further distillation over Na in a current of CO_2 , a mixture of hydrocarbons was obtained to the extent of 50.6% of theory, calculated on the basis of the α,β -unsaturated ketone. The hydrocarbon mixture was separated by fractionation into two fractions:

Fraction 1 - $149-157^\circ$ at 743 mm - 2.8 g, d_4^{20} 0.7801, n_D^{20} 1.4480.
Fraction 2 - $157-159^\circ$ - 4.2 g, d_4^{20} 0.7814, n_D^{20} 1.4498.

In this case, the ethyl radical had a large part to play in the dehydration of the tertiary alcohol. This led to the formation of the higher boiling 3,4,5-trimethylheptadiene-2,4. The 2-ethyl-3,4-dimethylhexadiene-1,3 was obtained in smaller quantity.

The synthesis from butylidene methylpropylketone and C_2H_5MgBr . ** Starting with 10 g butylidene methylpropylketone with b.p. $183-187^\circ$ at 729 mm and twice the theoretically necessary amount of C_2H_5MgBr , the synthesis was carried out in 100 ml of absolute ether at -10° . There was obtained 2.4 g of hydrocarbon with b.p. $166-168^\circ$ at 732 mm, d_4^{20} 0.7790, n_D^{20} 1.4529.

Found: MR_D 52.78.
 $C_{11}H_{20}$ Γ_2 . Calculated: MR_D 52.06

The yield of diene amounted to 20.5% of theory. It was not possible to determine the structure of the diene, which might have been either 4-ethylnona-diene-3,5 or 3-propyloctadiene-2,4. The only reactions carried out with the substance were bromination and the introduction of the iodoxy group.

*With the aid of laboratory worker M. V. Bobrova

**With the aid of student V.V. Molchanova

3. The Production of 2,3-Dimethylbutadiene-1,3 and Its Behavior upon Bromination

The 2,3-dimethylbutadiene-1,3 was prepared by two methods: 1) from pinacone by way of its dibromide, with the splitting off from the latter of the elements of HBr as a result of distillation with quinoline; 2) from pinacone by dehydration with KHSO_4 .

The preparation of diisopropenyl (a) obtained by the first method had a b.p. of 69-70° at 759 mm, d_4^{20} 0.7168; n_D^{20} 1.4215, M_R 29.075. The 4,5-dimethyl cyclohexene-4-dicarboxylic acid-1,2 obtained from the adduct has a m.p. of 205°; analysis of its Ag salt, dried at 85°, gave the following results:

0.2300 g substance: 0.1202 g Ag.

Found %: Ag 52.26.

$\text{C}_{10}\text{H}_{12}\text{O}_4\text{Ag}_2$. Calculated %: Ag 52.38.

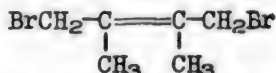
The preparation of diisopropenyl (b) obtained directly from pinacol had a b.p. of 69.5° at 746 mm, d_4^{20} 0.7206, n_D^{20} 1.4360. Upon treating 1 g of diisopropenyl with 1.7 g of maleic anhydride in 20 ml of toluene with heating for 20 hours so that the solution boiled gently, there was attained an adduct which was transformed into 2.3 g of 4,5-dimethylcyclohexene-4-dicarboxylic acid-1,2, with m.p. 202-203°. Analysis of its Ag salt gave the results:

0.2120 g substance: 0.1117 g Ag.

0.2432 g substance: 0.1279 g Ag.

Found %: Ag 52.68, 52.59.

The preparations of diisopropenyl (a) and (b) were brominated with the separation of little HBr, each molecule of the diene consuming about one molecule of bromine; this forced us to assume that the dibromide consisted basically of the 1,4 derivative:



In order to show the structure of the dibromide, it was made from 2.3 g of diisopropenyl and 6.2 g of bromine in CCl_4 solution at -15°. After the CCl_4 was driven off in vacuum at a bath temperature of 35-40°, the dibromide, which remained as a light brown liquid, was immediately dispersed in 20 ml of water and 150 g of finely pulverized ice, and during the course of a half hour 8 g of finely powdered KMnO_4 was added in three portions. The reaction mixture was energetically shaken. The flask was further allowed to stand overnight in the refrigerator. The KMnO_4 was completely reduced. The neutral oxidation products were distilled off with steam and appeared in the form of a viscous, colorless oil with strong lachrymatory properties. The aqueous distillate was saturated with NaCl and the organic products extracted with ether. The ether extracts were dried with anhydrous Na_2SO_4 . After separation of the Na_2SO_4 , the ether was distilled off and the residue fractionated. There was obtained 3.5 g of a colorless liquid with b.p. 132-138° at 755 mm. This showed a positive reaction to halogen (according to Beilstein's method), a color reaction with bromacetone and m-dinitrobenzene in alcoholic NaOH, and had d_4^{20} 1.26.

The residue from the distillation of the neutral oxidation products was filtered to remove MnO_2 and after washing of the latter with boiling water, concentrated to a small volume. The solution gave an alkaline reaction. After acidification with dilute H_2SO_4 , the organic acids were distilled off. The 1st fraction was 10 ml of aqueous distillate, the 2nd fraction 4 ml. The 1st fraction gave a positive reaction for formic acid and contained negligible traces of HBr.

With the aid of assistant V. V. Sergovskaya.

In order to neutralize 1 ml of this fraction, there was needed on an average 8.88 ml of 0.1 N NaOH solution, which corresponded to a content in 10 ml of distillate of 0.408 g of HCOOH. The 2nd fraction showed a very weak positive reaction for HCOOH and a stronger reaction for HBr.

In view of the amounts of bromacetone and HCOOH obtained by oxidation of the diisopropenyl dibromide, we must assume that the dibromide consisted chiefly (>75%) of the 1,4 derivative.

4. The bromination of portions of the diene hydrocarbons was carried out in a solution of 10 ml of dry CCl_4 cooled to 0° ; after the addition of a Br-CCl_4 solution, the reaction flasks were maintained at 0° for 30 minutes. The amounts of bromine used and of HBr separated were studied, in accordance with the directions of the MacIlliney method.

5. The introduction of the iodoxy group into portions of the hydrocarbons was carried out in a solution of 20 ml alcohol; after addition of the iodine-alcohol solution, mixing, the addition of 200 ml of water, and energetic shaking, the reaction mixture was allowed to stand for 5 minutes. The iodine used up and the amount of HI separated were studied according to the directions of the Margoshes method. In Tables 1, 2, and 3, for the purpose of brevity, 50% of the experimental data are given.

Table 4
Values of the parachors of diene hydrocarbons

No.	Name of the diene hydrocarbon	Molecular weight	d_4^{20}	Surface Tension	Parachor		% of difference
					Theor.	Found	
1	2,4-dimethylhexadiene-2,4.....	110.1	0.7542	23.98	324.2	323.0	0.4
2	2,3,4-trimethylhexadiene-1,3..	124.2	0.7701	25.15	363.2	361.3	0.5
3	3-methyl-5-ethylheptadiene-3,5	138.2	0.7710	24.79	402.2	400.0	0.5
4	2,6-dimethyloctadiene-4,6.....	138.2	0.7741	25.44	402.2	400.9	0.3
5	2,4-dimethylpentadiene-1,3....	96.1	0.7430	21.75	285.2	279.3	2.1
6	2-Tert.-butyl-4,5,5-trimethylhexadiene-1,3.....	160.3	0.7872	23.50	519.2	504.3	2.9
7	2-Methylheptadiene-1,3.....	110.1	0.7435	23.30	324.2	325.3	0.3
8	2,3-Dimethylbutadiene-1,3.....	82.1	0.7255	20.60	246.2	240.7	2.2
9.	4-Ethylnonadiene-3,5 or 3-propyloctadiene-2,4.....	152.2	0.7790	24.38	441.2	434.1	1.6

Parachors were determined for the series of diene hydrocarbons synthesized in our laboratory. Prof. S.G.Mokpushin directed aspirant T.P. Bolan in this work (Table 4).

Surface tension was determined by the method of blowing bubbles of air through the liquid.

SUMMARY

1. The following newly synthesized diene hydrocarbons have been described: 2,6-dimethylheptadiene-1,3; 3-methyloctadiene-2,4; 2-tert.-butyl-4,5,5-trimethylhexadiene-1,3; 2,3,4-trimethylhexadiene-1,3.

2. More precise physico-chemical constants have been found for 2,6-dimethyloctadiene-4,6; an improved yield of 2,4-dimethylpentadiene-1,3 has been obtained.

3. Grignard reactions have been studied for the systems: 1) 3-methylpentene-3-one-5 and CH_3MgI ; 2) 3,4-dimethylhexene-3-one-5 and $\text{C}_2\text{H}_5\text{MgBr}$; and 3)

butylidenemethylpropylketone and C_2H_5MgBr .

4. The following tertiary alcohols have been described: 2,6-methyloctene-4-ol-6 and 3,4,5-trimethylpentene-4-ol-3.

5. It has been shown that in the dehydration of α,β -unsaturated tertiary alcohols having the groups CH_3 and C_2H_5 attached to the carbinol carbon atom, the H atoms of the ethyl play the role.

6. With an equal number of radicals of an identical chemical nature attached to the carbons of the conjugated system, their effectiveness in decreasing the degree of conjugation is stronger the less symmetrical their arrangement in the system.

7. As the number of quaternary carbon atoms composing the skeleton of the conjugated system increases, the degree of conjugation of the ethylene bonds decreases, or, what amounts to the same thing, the independence of the ethylene bonds increases.

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Received September 9, 1947.

SYNTHESIS OF OLEFIN, PARAFFIN AND CYCLOPARAFFIN HYDROCARBONS

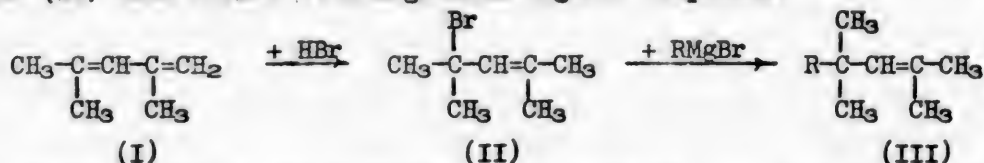
VII. TRANSFORMATION OF DIENES INTO CYCLOPROPANES. SYNTHESIS OF 1, 1, 2, 2-TETRAMETHYL CYCLOPROPANE

R. Ya. Levina, B. M. Gladshtein and P. A. Akishin

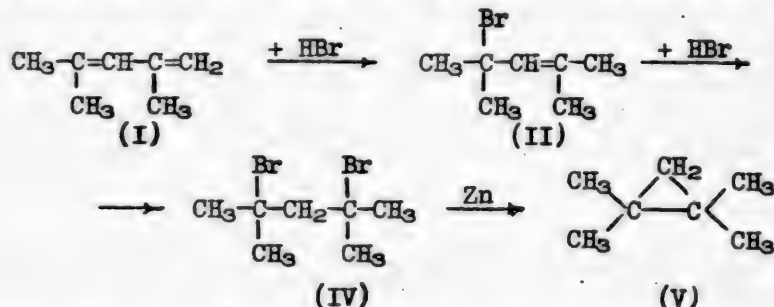
Academician N. D. Zelinsky Laboratory of Organic Chemistry of the Moscow State University, decorated with the Order of Lenin.

In previous communications by one of us [1-4] there have been descriptions of the application of the diene hydrocarbon with a conjugated system of double bonds, 2,4-dimethylpentadiene-1,3, to the synthesis of ethylene hydrocarbons containing a quaternary carbon atom.

The synthesis consisted of two steps - the addition of a molecule of hydrogen bromide to the 2,4-dimethylpentadiene-1,3 (I) and the reaction of the hydrobromide (II) thus formed with magnesium organic compounds:



Investigation of the unsaturated hydrocarbons (III) thus obtained revealed their structure, and consequently, the structure of the hydrobromide of 2,4-dimethylpentadiene-1,3, as well, the latter being a tertiary unsaturated bromide, a homolog of allyl bromide. Like the hydrobromide of piperylene [5], the hydrobromide of 2,4-dimethylpentadiene-1,3, due to the peculiarity of its structure, exists in only a single form, in contrast to other homologs of allyl bromide, which are capable of undergoing the allyl rearrangement. In this case, if the further addition of hydrogen bromide to this hydrobromide (II) took place in accordance with Markovnikov's rule, exhaustive hydrobromination of 2,4-dimethylpentadiene-1,3 (I) would lead to the formation of the bitertiary dibromide (IV), whose reaction with zinc dust would serve as a method for the preparation of the cyclopropane hydrocarbon (V), with two quaternary carbon atoms:



This reaction has been investigated in the present work.

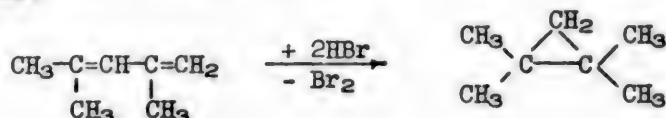
The experimental data obtained permit us to conclude with certainty that the addition of the two molecules of hydrogen bromide to the 2,4-dimethylpentadiene-1,3 takes place (under the reaction conditions utilized) exactly in accordance with the scheme given above, i.e., with the formation of the bitertiary dibromide (IV);

the action of zinc dust converts this dibromide into the hydrocarbon, whose three-membered cyclic structure was confirmed on the basis of its physical properties (constant of molecular refraction, parachor, and spectrum of combined scattering of light) as well as by means of its chemical transformation. The hydrocarbon did not decolorize and acidified solution of potassium permanganate, and only slowly decolorized a solution of bromine in chloroform. It polymerized easily upon treatment with concentrated sulfuric acid and aluminum chloride. Diluted sulfuric acid (80%), which easily reacts with ethylene hydrocarbons, had practically no effect upon this hydrocarbon.

A comparison of the physical and chemical properties of the hydrocarbon showed without any doubt that it was 1,1,2,2-tetramethylcyclopropane, i.e., that it had the structure that followed from the method of its synthesis. The yield of tetramethylcyclopropane attained 60-70% of the theoretical, calculated on the basis of the diene hydrocarbon treated with hydrogen bromide.

The availability of the initial diene hydrocarbon, the high yield of cyclopropane hydrocarbon, the simplicity with which the reaction itself can be carried out (see above scheme) without the separation of its intermediate products [the unsaturated hydrobromide (II) and the dihydrodibromide (IV)] permit us to consider this reaction as a new, simple, and convenient method for the preparation of various homologs of cyclopropane.

This reaction permits us to carry out a new, previously unknown, direct transition from the aliphatic hydrocarbon with a conjugated system of double bonds to the homolog cyclopropane with the same number of carbon atoms, and thus, for the first time, to show the relation between these two different types of hydrocarbons:



EXPERIMENTAL

The compound 2,4-dimethylpentadiene-1,3 (I) was synthesized (with a yield of 58% of the theoretical) by the reaction of mesityl oxide with methyl magnesium iodide according to the method described in detail in one of the previous communications [4]. The hydrocarbon had the following constants:

B.p. 92-93° (750 mm); n_D^{20} 1.4448; d_4^{20} 0.7376; MR_D 35.69.
 C_7H_{12} 2. Calculated MR_D 33.59; EM_D 2.10.

The addition of hydrogen bromide to 2,4-dimethylpentadiene-1,3. Dry hydrogen bromide, purified of traces of bromine, was led into the reaction vessel containing 20 g of dimethylpentadiene, which was cooled with a mixture of snow and salt, until the weight reached 31 to 32 g. The addition of hydrogen bromide was completed in 40 to 45 minutes. The dihydrodibromide of 2,4-dimethylpentadiene-1,3 obtained, (IV), was not separated from the reaction mixture, but brought into reaction with zinc dust directly after being obtained.

Reaction of the dihydrodibromide of 2,4-dimethylpentadiene-1,3 with zinc dust — the production of 1,1,2,2-tetramethylcyclopropane. The first experiments on the action of zinc dust with the dibromide obtained led to the splitting off of two molecules of hydrogen bromide, and the formation of the initial dimethylpentadiene with b.p. 92-93°, and in part, of its dimer [1] with b.p. 217-219°. In these experiments, the dibromide, immediately after it was obtained, was added to the zinc dust, which was covered with 80% alcohol, and the reaction mixture was not cooled. In the following experiments, the dibromide was cooled (in a

dropping funnel) to a point close to its solidification temperature, and the reaction mixture cooled with a mixture of snow and salt. These conditions guaranteed the stability of the bitertiary dibromide, and the product of its reaction with zinc dust was shown to be the cyclopropane hydrocarbon.

After a series of experiments with various conditions for carrying out the reaction and separating its products, a method was worked out for obtaining the cyclopropane hydrocarbon (V) with a yield of 60% of the theoretical. This method is described below.

The reaction was carried out in a three-necked flask, fitted with a stirrer with mercury seal, a dropping funnel (with a jacket for cooling with ice), and a dephlegmator (30 cm high) joined to a descending condenser. To 60 g of zinc dust and 100 g of alcohol (96%) with energetic stirring, and cooling with an ice-salt mixture, there was slowly added an alcoholic solution of the dibromide (cooled in the dropping funnel with ice or ice water)* directly upon its production from the 20 g of dimethylpentadiene.

After the introduction of the dibromide was complete, the reaction mixture was stirred for 2 more hours with cooling, 5 to 6 hours (on the following day) at room temperature, and 1 hour with heating on the water bath. Then the fraction boiling at 58 to 78° (25 to 30 ml) was distilled off. This consisted of a mixture of the alcohol with the hydrocarbon, from which the latter was separated out by the addition of water. The hydrocarbon was twice washed with water, dried with calcium chloride, and distilled with a dephlegmator over metallic sodium. The fraction boiling from 75 to 76° was collected (its yield reached 12 to 13 g, i.e., 60% of the theoretical on the basis of the dimethylpentadiene used). The hydrocarbon obtained contained no halogen (Beilstein test), did not decolorize an acid solution of permanganate, and very slowly (after several minutes) decolorized a solution of bromine in carbon tetrachloride. After distillation through a column (theoretically equivalent to 30 plates) the hydrocarbon had the following constants:

B.p. 75° (747 mm); n_D^{20} 1.4010; d_4^{20} 0.7188; MR_D 33.18.

C_7H_{14} . Calculated: MR_D 32.32; EM_D 0.86.

Aniline point 51.25 (maximum aniline point the same).

According to the literature data, the exaltation of the molecular refraction for homologs of cyclopropane equals 0.7 [8] or 0.8 [7].

4.325 mg substance: 13.566 mg CO_2 ; 5.570 mg H_2O .

4.650 mg substance: 14.583 mg CO_2 ; 5.995 mg H_2O .

Found %: C 85.60, 85.58; H 14.41, 14.42.

C_7H_{14} . Calculated %: C 85.62; H 14.38.

Determination of parachor [8]:

δ_{20} 20.86, 20.41.

Found P: 289.67, 290.1

C_7H_{14} with three-membered ring. Calculated (according to Sugden) P 289.7.

Investigation of the spectrum of combined scattering of light of hydrocarbon (V).** The spectrum of combined scattering was obtained by a 'Shteinkhel' spectrograph with dispersion 9 Å/mm in the region λ 4350 Å and 17 Å/mm in the region

*After completion of the reaction between hydrogen bromide and 2,4-dimethylpentadiene, the dibromide obtained was dissolved in an equal volume of 96% alcohol and this solution used for the reaction. Upon strong cooling (ice and salt) the alcohol solution separated into layers, and the lower layer of dibromide crystallized.

**We wish to utilize the occasion to express our thanks to V. M. Tatevski for his aid and advice in the spectroscopic investigations carried out in the present work.

λ 4900 Å. To stimulate the spectrum, the mercury line at 4358 Å was utilized, separated from the short-wave part of the mercury spectrum by a filter of a saturated solution of potassium nitrite. The spectrum was recorded on an Ilford plate with sensitivity 555 M₂D at three-hour exposure. The width of the aperture of the spectrograph corresponded to 6 cm⁻¹ on the spectrum. The temperature at which the material was measured was maintained within the limits of 20 to 30°.

Below are given the frequencies of the spectrum of combined light scattering of light for the hydrocarbon C₇H₁₄; in parentheses are given the relative intensities in arbitrary units, estimated approximately by means of the height of the corresponding peaks on the microphotogram.

318(6.5), 373(15), 397(10), 414(8), 455(5), 484(4.5), 661(36), 690(32.5), 860(34), 895(13), 943(17), 1028(21.5), 1125(18), 1201(16), 1216(5), 1296(12), 1354(33), 1376(23.5), 1397(20.5), 1449(34), 1462(20), 1483(6), 2731(3.5), 2880(23), 2930(26.5), 2949(22.5), 2992(20.5), 3055(6).

A number of authors [9] have demonstrated the following peculiarities in the spectra of combined scattering of cyclopropane hydrocarbons: 1) the spectra of cyclopropane and its homologs have frequencies between 3064 and 3076 cm⁻¹; 2) the spectra of alkylcyclopropanes [10] have strong frequencies in the interval from 1207 to 1221 cm⁻¹, permitting their use in the identification of this type of structure [11,12]; 3) a theoretical calculation [13,14] of the frequencies of cyclopropane on the basis of a trinuclear triangular model shows that the main frequencies of the carbon bonds must be approximately in the ratio $1:\sqrt{2} = 1:1.41$. This corresponds satisfactorily to the experimental data [10], presented in Table 1.

Table 1
Ratios between the frequencies of the carbon skeleton
for hydrocarbons of the cyclopropane series.

Hydrocarbon	Frequency in the range		Average value		
	1200 cm ⁻¹ (ω_1)	850-950 cm ⁻¹ (ω_2)	ω_1	ω_2	$\frac{\omega_1}{\omega_2}$
Cyclopropane.....	1188	867	1188	867	1.37
Methylcyclopropane.....	1207	851, 892	1207	871.5	1.39
1,2-Dimethylcyclopropane...	1214	866, 915	1214	890.5	1.36
1,2-Methylethylcyclopropane	1209, 1221	786, 957	1214	871.5	1.39
1,2-Methylpropylcyclopropane.....	1207, 1221	786, 957	1214	871.5	1.39
1,1,2,2-tetramethylcyclopropane, obtained in the present work.....	1201, 1216	860, 895	1208.5	877.5	1.38

From a comparison of the data given in the literature and the spectral frequencies of the hydrocarbon obtained by us, we may draw the following conclusions: 1) the line 3055 cm⁻¹, in the absence of the frequency 1600 cm⁻¹ (C=C) may be ascribed only to the bond C-H in the cyclane; 2) the groups of frequencies 1201(16), 1216(5) and 860(34), 895(13) lie in the frequency range of the C-C of cyclopropanes, and between them, the characteristic ratio $1:\sqrt{2}$ is preserved. These data confirm the presence of a three-membered ring in the hydrocarbon obtained by us.

Thus, on the basis of analysis, and the constants for the exaltation of the molecular refraction, the parachor, and the spectra of combined scattering of light we can with complete certainty ascribe to the hydrocarbon obtained the

structure of the 1,1,2,2-tetramethylcyclopropane resulting from the method of its synthesis.

The chemical properties of tetramethylcyclopropane. Action of sulfuric acid (80%). A 2 ml sample of 1,1,2,2-tetramethylcyclopropane was treated with agitation (30 minutes) in a graduated cylinder with an equal volume of 80% sulfuric acid; 0.3 ml of hydrocarbon was absorbed. After separation from the sulfuric acid, washing, and drying, the hydrocarbon was distilled over sodium. It distilled over entirely at 75°, and had the constants of the original hydrocarbon, (n_D^{20} 1.4020; d_4^{20} 0.7190). Thus, 80% sulfuric acid, which reacts with ethylene hydrocarbons, had practically no effect on the cyclopropane hydrocarbon.

The action of concentrated sulfuric acid. 2.2 ml of the tetramethylcyclopropane was treated with agitation and cooling to room temperature (30 minutes) in a graduated cylinder with an equal volume of concentrated sulfuric acid; 0.5 ml of hydrocarbon was absorbed. The separated hydrocarbon layer was washed until it gave a neutral reaction, dried over calcium chloride, and distilled over sodium. It boiled within the range 240 to 260 and had n_D^{20} 1.4520. The fraction obtained was a viscous liquid with an unsaturated character (according to the reaction with potassium permanganate). Thus, concentrated sulfuric acid shows a polymerizing effect on tetramethylcyclopropane.

Action of aluminum chloride. The reaction between tetramethylcyclopropane and aluminum chloride was carried out with energetic mechanical stirring; the aluminum chloride was added gradually to the hydrocarbon. After decomposition of the reaction mixture with water, the hydrocarbon layer which separated out was washed until it gave a neutral reaction, dried, and distilled over sodium. The results of different experiments, conducted under various conditions (temperature of the reaction, duration of experiment, presence of a solvent) are given in Table 2.

Table 2

Action of aluminum chloride on tetramethylcyclopropane

Tetramethylcyclopropane (g)	Aluminum chloride (g)	Solvent	Rise in temp of the reaction mixture during addition of aluminum chloride	Continuation of stirring after addition of Aluminum chloride and temp. of reaction mixture	Properties of the products of reaction		
					B.p.	n_D^{20}	Behavior toward potassium permang.
10	4.5	—	To 64°	15 hours (20°)	170-220° (50 mm)	1.4720	decolorizes
5	2.25	—	Cooling to 4-5°	1 hour (4°)	75° (2.5 g) viscous residue	1.4015	does not decolorize
5	2.25	carbon disulfide (20 ml)	To 31°	—	75-75.5° (2.5 g) viscous residue	1.4015	does not decolorize

The experiments listed on the action of aluminum chloride upon the tetramethylcyclopropane permit us to conclude that, depending upon the conditions of reaction, the tetramethylcyclopropane either completely polymerizes, or, under less drastic conditions, is partly converted into a stable form.

SUMMARY

1. A method has been devised for obtaining cyclopropane hydrocarbons by the three following steps: synthesis of the diene hydrocarbon with a conjugated system of double bonds, addition to it of two molecules of hydrogen bromide, and the splitting off from the dibromide formed of two atoms of bromine. Thus, a new, formerly unknown method of going over from the aliphatic diene hydrocarbon to a cyclopropane homolog with the same number of carbon atoms has been worked out.

2. By this method there has been synthesized (with a yield of 60% of the theoretical, calculated on the original diene hydrocarbon) a homolog of cyclopropane with two quaternary carbon atoms. This compound, which is not described in the literature, is 1,1,2,2-tetramethylcyclopropane. Its structure has been confirmed by a study of its physical and chemical properties: exaltation of the molecular refraction, parachor, the presence of characteristic frequencies in the spectrum of combined scattering of light, behavior to potassium permanganate, bromine, dilute and concentrated sulfuric acid, and aluminum chloride.

For the first time, there has been shown the possibility of utilizing a bitertiary 1,3-dibromide in the Gustavson reaction.

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Received January 5, 1948.

CHEMICAL EQUILIBRIUM IN REACTIONS BETWEEN HYDROCARBONS

EQUILIBRIUM OF THE REACTION: $\text{iso-C}_3\text{H}_7\text{C}_6\text{H}_5 + 3\text{H}_2 \rightleftharpoons \text{iso-C}_3\text{H}_7\text{C}_6\text{H}_{11}$



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The present article contains the results of our work performed in 1947. It is the logical continuation of our investigations in the field of the equilibrium of organic reactions, and in particular, of the hydrogenation reactions of aromatic hydrocarbons [1].

Method of work: To determine the equilibrium constants, we utilized an arrangement of apparatus, assembled according to the scheme described in the article of Zharakova and Frost [7], with the difference that for a thermostatic liquid we utilized machine oil. The thermostat in which the vaporizer was placed was also filled with oil.

Catalyst. As catalyst of the hydrogenation reaction of the aromatic hydrocarbons, isopropylbenzene and 1,3-dimethylbenzene (m-xylene), from which the corresponding hydroaromatic hydrocarbons were obtained, we used metallic nickel, with a kieselguhr carrier.

Initial preparations. Hydrogen was obtained from the "Salolin" factory; it contained 95 to 98% H_2 and 2 to 5% N_2 .

Isopropylbenzene was obtained from technical isopropylbenzene by means of a triple distillation from a Wurtz flask with a herringbone dephlegmator. The fraction boiling in the interval 152-153° was separated and dried over calcium chloride.

Isopropylcyclohexane was obtained by the hydrogenation of the above-indicated isopropylbenzene over nickel catalyst at atmospheric pressure and a temperature of 180-200°. The preparation thus obtained was washed three times with 98% sulfuric acid to which 2 to 5% of P_2O_5 had been added, carefully washed with water, and dried over calcium chloride.

The 1,3-dimethylbenzene (m-xylene) was prepared from technical xylol by sulfonation and subsequent high-temperature hydrolysis of the sulfonic acid, according to Kizhner's method [2]. It was then washed and dried over calcium chloride.

The 1,3-dimethylcyclohexane was prepared in the same manner as the isopropylcyclohexane, by the hydrogenation of m-xylene over nickel in the manner indicated above.

The physical chemical constants of the hydrocarbons utilized in our work are listed in Table 1. For purposes of comparison, we have also listed the data taken from Doss's handbook [3].

The data in these tables indicate that the physical chemical constants of the hydrocarbons prepared by us are in good agreement with the figures given in the literature. In addition, it appears that the 1,3-dimethylcyclohexane utilized by us was, in all probability, to judge from its constants, a mixture of the cis- and trans-isomers.

The results of specially performed preliminary experiments showed that the hydrogenation of isopropylbenzene and m-xylene took place practically without side reactions at temperatures up to 250°; we therefore considered it possible to determine the composition of the hydrogenated mixture by a refractometric method.

For this purpose, we prepared artificial mixtures, and then determined their coefficients of refraction. Results of these measurements are listed in Table 2.

In Fig. 1 we have compared our measurement of the refractive indices of the binary mixtures of m-xylene and 1,3-dimethylcyclohexane with the measurements made by Lozovoi, Dyakova, and Stepanseva [4].

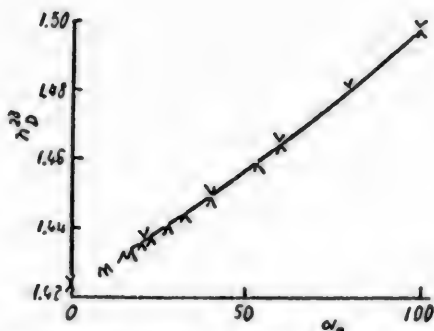
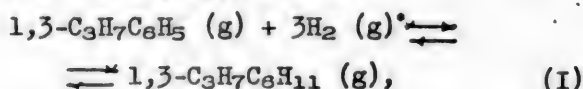


Fig. 1. Indices of refraction (n_D^{20}) of the binary mixtures: m-xylene and 1,3-dimethylcyclohexane.

Symbols used: V - our data; A - data of Lozovoi and others [4]

For convenience in the work, on the basis of the data given here, we constructed Table 3, in which the indices of refraction of the binary mixtures are calculated for every 2%.

Results of the measurements of the equilibrium constant of the hydrogenation reaction of isopropylbenzene:



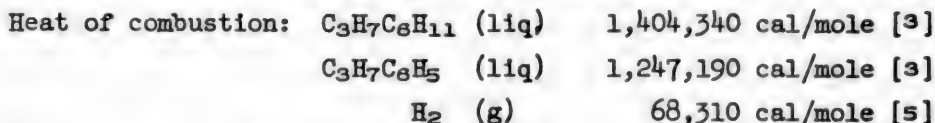
are given in Table 4.

The gas leaving the reactor was analyzed for its content of hydrogen, methane, and nitrogen. These analyses showed that only during hydrogenation above 250° did the reaction gas contain less hydrogen than might have been expected (the admixture consisted of methane and nitrogen). In the experiments carried out at a temperatures below 250°, the content of methane and nitrogen in the gas from the reaction increased after the experiment in strict proportionality to the decrease in the volume of gas, showing a relation to the consumption of hydrogen in hydrogenation.

Table 1
Comparison of physical chemical constants of hydrocarbons used in our work with data in the literature

Name of hydrocarbon	B.p. under normal conditions		Specific gravity d_4^{20}		Index of refraction n_D^{20}	
	Our data	Doss	Our data	Doss	Our data	Doss
Isopropylbenzene.....	152-153°	152.4	0.8626	0.8615	1.4895	1.4912
Isopropylcyclohexane.....		154.4	0.8040	0.8016	1.4412	1.4408
m-Xylene	139-139.5	139.2	0.863	0.864	1.4965	1.4971
1,3-Dimethylcyclohexane.....			0.7707		1.4238	
1,3-Dimethylcyclohexane-cis...		124.7		0.7845		1.4310
1,3-dimethylcyclohexane-trans.		120.7		0.7661		1.4230

The calculation of the equation relating $\lg K_p$ to the temperature was carried out with the aid of the following thermochemical values:



In consequence of the lack of data on the heat of combustion of isopropylcyclohexane in the vapor phase, we were forced to calculate the heat of the

* (g) refers here and hereafter to Gas.

Table 2

Experimental data on measurements of specific gravity d_4^{20} and index of refraction n_D^{20} of the binary mixtures:

m-xylene - 1,3-dimethylcyclohexane and isopropylbenzene - isopropylcyclohexane

Weight percent		d_4^{20} according to data of:		n_D^{20} according to data of:		Wt. % isopropylbenzene	n_D^{20} our data
m-Xylene	1,3-dimethylcyclohexane	Lozovoi et al. [4]	Our data	Lozovoi et al. [4]	Our data		
100	—	0.8641	0.8630	1.4974	1.4965	100	1.4895
79.75	20.25	0.8435	—	1.4802	—	90.94	1.4850
60.13	39.87	0.8234	—	1.4650	(1.4637)	73.44	1.4750
53.37	46.63	—	—	—	1.4591	51.57	1.4642
44.54	55.46	—	—	—	1.4532	41.02	1.4595
39.78	60.22	0.8033	—	1.4502	(1.4498)	36.49	1.4573
32.78	67.22	—	—	—	1.4441	32.49	1.4565
28.21	71.79	—	—	—	1.4415	28.12	1.4535
22.89	77.11	—	—	—	1.4376	27.01	1.4532
20.23	79.77	0.7859	—	1.4370	(1.4363)	21.61	1.4511
16.80	83.20	—	—	—	1.4340	20.83	1.4500
15.36	84.64	—	—	—	1.4330	15.64	1.4485
11.68	88.32	—	—	—	1.4305	10.27	1.4462
9.68	90.32	—	—	—	1.4295	9.36	1.4452
7.24	92.76	—	—	—	1.4280	7.60	1.4450
6.83	93.17	—	—	—	1.4278	4.12	1.4430
2.96	97.04	—	—	—	1.4250		
—	100	0.7677	0.7707	1.4240	1.4235		

(Note: Figures in parentheses were obtained by graphic interpolation.)

Table 3

Calculated values of indices of refraction (n_D^{20}) for the binary mixtures:
m-xylene - 1,3-dimethylcyclohexane and isopropylbenzene - isopropylcyclohexane

Weight percent	n_D^{20}		Weight percent	n_D^{20}	
	isopropylbenzene	m-xylene		isopropylbenzene	m-xylene
0	1.4410	1.4235	32	1.4552	1.4444
2	1.4419	1.4246	34	1.4561	1.4458
4	1.4428	1.4258	36	1.45706	1.4472
6	1.4437	1.42705	38	1.45795	1.44855
8	1.44454	1.4283	40	1.4589	1.4496
10	1.4454	1.4296	42	1.4598	1.4513
12	1.44625	1.4309	44	1.4607	1.45265
14	1.4471	1.4322	46	1.4616	1.4540
16	1.4480	1.4335	48	1.4625	1.45535
18	1.4489	1.43485	50	1.4634	1.45675
20	1.4498	1.4362	52	1.4644	1.4581
22	1.4507	1.4375	54	1.4655	1.4595
24	1.4516	1.4388	56	1.4665	1.4609
26	1.4525	1.4402	58	1.4676	1.4623
28	1.4534	1.4416	60	1.4687	1.4637
30	1.4543	1.4430			

hydrogenation reaction of isopropylbenzene from the heat of combustion of the liquid normal propylbenzene and propylcyclohexane.

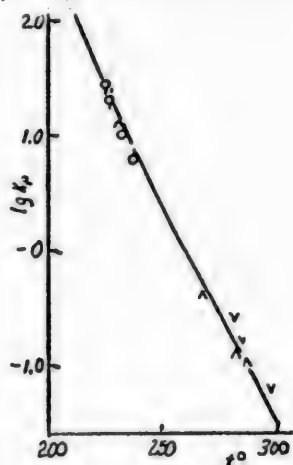


Fig. 2. Numerical values of $\lg K_p$ for the hydrogenation reactions of n-propylbenzene and isopropylbenzene found experimentally (points) and calculated from Equation (1) (curve).

Symbols used: \circ - isopropylbenzene;
 ∇ - n-propylbenzene.

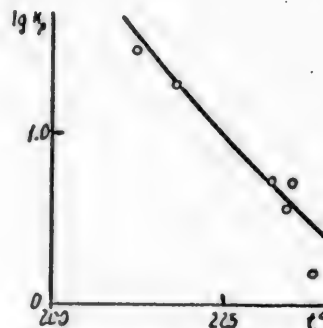


Fig. 3. Numerical values of $\lg K_p$ for the hydrogenation reaction of m-xylene.

symbols used: \circ - experimental data;
 curve - calculated from equation (2).

In order to determine the dependence of the heat effect of the reaction in $\lg K_p$ on the temperature, we assumed:

$$\text{for iso-C}_3\text{H}_7\text{C}_6\text{H}_{11} \text{ (g): } C_p = -8.426 + 0.1819T - 0.00007276T^2$$

$$\text{for iso-C}_3\text{H}_7\text{C}_6\text{H}_5 \text{ (g): } C_p = -7.394 + 0.1559T - 0.00006250T^2$$

$$\text{for H}_2 \text{ (g): } C_p = 6.744 + 0.0002774T + 0.0000001956T^2$$

These equations were calculated by us according to the method of Benewitz and Rosner [8].

The equation for the dependence of the heat capacity of hydrogen on the temperature was calculated by us according to the method of least squares from the data of Wagmann, Kilpatrick, Taylor, Pitzer, and Rossini [5].

From the data given above:

$$\Delta H_{298} = -47790$$

$$\Delta H_0 = -42830 \text{ and}$$

$$\lg K_p = \frac{9365.8}{T} - 10.707 \lg T + 0.0036265T - 0.000000395328T^2 + 9.8 \quad (1)$$

The constant 9.8 in equation (1) was calculated on the basis of our experimental data.

This equation agrees comparatively well with the experimental data both for the hydrogenation of n-propylbenzene and of isopropylbenzene (Table 5). Only in isolated instances does the deviation in $\lg K_p$ reach 0.15.

Table 4
Results of experimental measurements of the equilib. constant for the reaction:
 $\text{iso-C}_3\text{H}_7\text{C}_6\text{H}_5 \text{ (g)} + 3\text{H}_2 \text{ (g)} \rightleftharpoons \text{iso-C}_3\text{H}_7\text{C}_6\text{H}_{11} \text{ (g)}$

No. of expt.	Temperature of reaction °C	Starting Material	n_D^{20} of mixture	% $\text{C}_3\text{H}_7\text{C}_6\text{H}_{11}$ in mixture	lg K_p	
					experimental	Calculated according to Equation (1)
1	205°	$\text{C}_3\text{H}_7\text{C}_6\text{H}_5$	1.4452	89.77	1.82	
2	223	same	1.4515	76.20	1.23	
3	227	90% $\text{C}_3\text{H}_7\text{C}_6\text{H}_{11}$	1.4458	89.0	1.31	1.35
4	231.5	same	1.4485	83.0	1.01	1.15
5	237	same	1.4525	74.0	0.80	0.91
6	225	$\text{C}_3\text{H}_7\text{C}_6\text{H}_5$	1.4495	80.6	1.425	1.43
7	210	same	1.4437	94.0	(1.184)	
8	210	same	1.4430	95.5	2.15	2.11
9	204	same	1.4812	95.3	(0.55)	

Table 5
Experimental and calculated values of lg K_p for the reactions:
 $\text{iso-C}_3\text{H}_7\text{C}_6\text{H}_5 \text{ (g)} + 3\text{H}_2 \text{ (g)} \rightleftharpoons \text{iso-C}_3\text{H}_7\text{C}_6\text{H}_{11} \text{ (g)}$ according to data of present work;
 $\text{n-C}_3\text{H}_7\text{C}_6\text{H}_5 \text{ (g)} + 3\text{H}_2 \rightleftharpoons \text{n-C}_3\text{H}_7\text{C}_6\text{H}_{11} \text{ (g)}$ according to data of Vvedensky and others [1]

Line No.	Temperature of reaction		Starting Material	log K_p		Deviation
	t °C	T°K		Experi-mental	Calculated according to [1]	
1	210	483	iso- $\text{C}_3\text{H}_7\text{C}_6\text{H}_5$	2.15	2.11	- 0.04
2	225	498	same	1.425	1.435	+ 0.01
3	227	500	mixture in near equilibrium ratio	1.31	1.35	+ 0.04
4	231.5	504.5	iso- $\text{C}_3\text{H}_7\text{C}_6\text{H}_{11}$	1.01	1.15	+ 0.14
5	237	510	same	0.80	0.91	+ 0.11
6	231	504.1	n- $\text{C}_3\text{H}_7\text{C}_6\text{H}_5$	1.10	1.173	+ 0.073
7	267	540.1	same	-0.384	-0.272	+ 0.112
8	280.5	558.6	n- $\text{C}_3\text{H}_7\text{C}_6\text{H}_{11}$	-0.600	-0.767	- 0.167
9	282	555.1	n- $\text{C}_3\text{H}_7\text{C}_6\text{H}_5$	-0.866	-0.820	+ 0.046
10	284	557.1	n- $\text{C}_3\text{H}_7\text{C}_6\text{H}_{11}$	-0.826	-0.891	- 0.065
11	287	560.1	n- $\text{C}_3\text{H}_7\text{C}_6\text{H}_5$	-0.955	-0.997	- 0.042
12	297.5	570.6	n- $\text{C}_3\text{H}_7\text{C}_6\text{H}_{11}$	-1.24	-1.357	- 0.117

Table 6
Results of experimental measurements of the equilibrium constants of the reaction:
 $1,3\text{-(CH}_3)_2\text{C}_6\text{H}_4 \text{ (g)} + 3\text{H}_2 \text{ (g)} \rightleftharpoons 1,3\text{-(CH}_3)_2\text{C}_6\text{H}_{10} \text{ (g)}$

Expt. No.	Temperature of reaction °C	Starting material	n_D^{20} of mixture	Percent of 1,3-(CH ₃) ₂ C ₆ H ₁₀ in mixture	lg K_p	
					Exptl.	Calc. from Equation (2)
1	212	(CH ₃) ₂ C ₆ H ₄	1.4425	70.8	1.47	1.6
2	218	same	1.4455	66.5	1.28	1.3
3	232	same	1.4540	54.0	0.725	0.7
4	234	same	1.4580	48.1	0.565	0.65
5	235	same	1.4513	58.0	0.707	0.6
6	238	(CH ₃) ₂ C ₆ H ₁₀	1.4640	39.5	(0.192)	0.5

If in the comparisons of experimental values of K_p with those calculated from Equation (1), we take into consideration only those points obtained by working with a starting mixture of an approximately equilibrium composition (Fig. 2), as has been listed, for example, in the third line of Table 5, or the points obtained as the system approaches the equilibrium conditions from two sides, as for example, the experiments listed in lines nine and ten of the same table, then the difference between the experimental values of $\lg K_p$ and those calculated amounts in all to about $\pm 0.05\%$.

Thus, we can assume to a high degree of approximation that the deep hydrogenations of n-propylbenzene and isopropylbenzene in the range of temperature investigated are practically identical.

The results of our experiments on the measurement of the equilibrium constants of the hydrogenation action of m-xylene:



are given in Table 6 and Fig. 3.

The calculation of $\lg K_p$, on the basis of the experimental data given in Table 6, permits us to propose, as an expression of the dependence of $\lg K_p$ of reaction (II) on the temperature, the following empirical equation:

$$\lg K_p = - \frac{10970}{T} - 21.$$

SUMMARY

1. The equilibrium constants of the hydrogenation reaction of isopropylbenzene have been measured. An equation has been given for the dependence of $\lg K_p$ on the temperature.

2. The equilibrium constants of the equation for the hydrogenation reaction of m-xylene have been measured. An empirical equation has been proposed for the calculation of $\lg K_p$.

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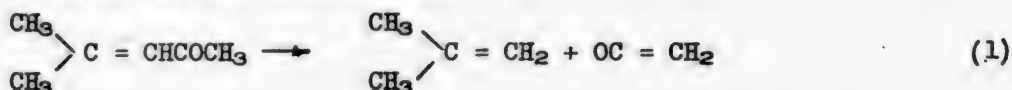
THE DECOMPOSITION OF MESITYL OXIDE ON ALUMINOSILICATE CATALYST

M. Ya. Kagan and R. I. Savachenko

In the work of M. Ya. Kagan and V. B. Falkovsky [1], it was shown that the formation of acetic acid from acetone in the presence of an aluminosilicate catalyst could be explained as the result of consecutive catalytic reactions: the condensation of acetone to give mesityl oxide, with the splitting off of water, and the cracking of the mesityl oxide with the formation of ketene and isobutylene. The ketene reacts with water, forming acetic acid. A similar cracking of mesityl oxide was observed by McAllister, Bailey, and Bouton [2] in the utilization of silicophosphate catalyst.

In the work of these authors, the mesityl oxide was passed over the catalyst at 300°, the products of reaction were condensed in a water-cooled condenser, and collected in a receiving vessel. The uncondensed vapors passed through a scrubber sprayed with water, where the reaction of the ketene with water took place. It appeared that no acid was observed in the first receiver, and that only the water used for scrubbing contained acetic acid - a product of the reaction of the ketene with water.

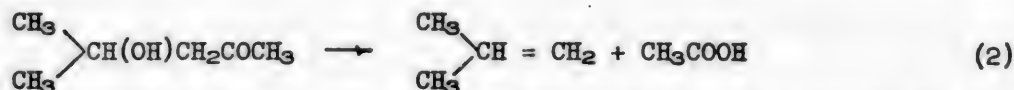
The equation for the reaction is:



Upon a single passage, 36% of the mesityl oxide was converted into acetic acid and isobutylene; 13% was converted during the following two passages, and 10% during the final two passages of the work. The average yield of acetic acid in carrying out the fivefold passage amounted to about 40% of the mesityl oxide converted.

The authors observe that during the catalytic decomposition of the mesityl oxide, there is a great deal of tar formation on the catalyst.

In the case where diacetone alcohol was passed through instead of mesityl oxide, there also took place the formation of acetic acid and isobutylene; but all the acetic acid was collected in the first receiver, and no ketene was removed in the scrubber:



At a temperature of 265°, the yield for a single passage amounted to 84 mol. % for acetic acid; 72 mol. % for isobutylene.

The catalyst was covered with a tarry polymer layer.

The same picture as in the case of the decomposition of diacetone alcohol was observed in the passage above a catalyst at 265° of a mixture of mesityl

oxide and water in the molar ratio of 1:1.6; in this case all the acetic acid was observed in the first receiver.

The conversion amounted to ~97%; approximately 94% of the mesityl oxide converted formed acetic acid and isobutylene, plus a small quantity of diisobutylene.

The equation for the reaction is:



On the basis of the fact that the conversion of mesityl oxide mixed with water (or of diacetone alcohol) is much greater than in the case of the contacting of dry mesityl oxide, the authors consider that two independent reactions for the conversion of mesityl oxide may be taking place on the silicophosphate catalyst: 1) catalytic splitting (cracking) according to equation (1) and 2) hydrolysis of the mesityl oxide according to equation (3), the second reaction taking place much more rapidly than the first.

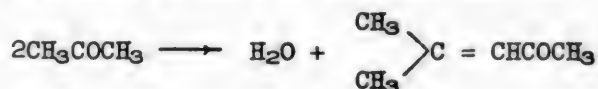
This conclusion, in our opinion, is in error because the authors did not taken into account the inhibiting role of the adsorbed polymers of ketene and isobutylene. We regard reaction (3) as consisting of two consecutive reactions [1], of which the first is the splitting of mesityl oxide (1), and the second the reaction between ketene and water:



If the splitting of mesityl oxide takes place in the absence of water, then, because of the polymerization of the ketene, the surface is contaminated, and the reaction is inhibited.

In this work of McAllister et al., the usual catalyst for isobutylene polymerization of the Standard Oil Company was utilized. This contains 60.4% of total phosphate in the form P_2O_5 and 25% of free phosphoric acid (H_3PO_4). To decrease the tendency to cause polymerization, the authors dried the catalyst for 50 hours at 110° , after which it contained 57% of total phosphate in the form of P_2O_5 and only 5% of free phosphoric acid. The catalyst, as was indicated, quickly lost its structure during the decomposition of pure mesityl oxide. During the decomposition of diacetone alcohol, the catalyst, according to the authors, was used for more than 50 hours. The great length of service, and the high yield during the decomposition of the easily dehydrated diacetone alcohol were explained by the fact that in the presence of water, which reacted with the ketene, the possibility of the formation of a polymer film was decreased, and high conversion was attained. This effect of avoiding inhibition by the products of the reaction often takes place in the case of consecutive reactions with heterogeneous catalysis [3].

In the present investigation we wished to supplement the work of Kagan and Falkovsky by a study of the cracking of mesityl oxide on an aluminosilicate catalyst in the presence of water, used in various proportions. We may note that during the passage of pure acetone over this sort of catalyst at 300° , water is always formed as a primary product of the condensation:



and therefore, the ketene, formed during the subsequent cracking of the mesityl

oxide, at once gives acetic acid. There are two layers of condensate in the receiver. We might expect that during contact decomposition of mesityl oxide, no water layer would be obtained, and that it would be possible to collect the ketene. It appeared, however, that a small water layer (concentrated solution of acetic acid) was always obtained in the condensate.

The mesityl oxide we used was synthesized by the method of Hoffman [4], by the condensation of acetone in the presence of calcium oxide to give diacetone alcohol. In view of the fact that at equilibrium the yield of diacetone alcohol in the aldol condensation does not exceed 14%, Hoffman's method provides for the continuous distillation of the acetone from the products of the reaction, and its passage in liquid form above a catalyst, located separately in a Soxhlet apparatus. Upon acidification of the diacetone alcohol with a few drops of sulfuric acid, and rectification, the mesityl oxide is obtained. After drying with calcium chloride and redistillation, mesityl oxide was obtained with d_4^{20} 0.8575; n_D^{20} 1.4440. Mesityl oxide and water were fed into a contact apparatus from two burettes at constant speed. The splitting of mesityl oxide took place in a contact tube, diameter 12 mm, volume of the catalyst layer 30 ml. The catalyst was a technical synthetic aluminosilicate catalyst, produced in the Soviet Union for cracking purposes.

The products of reaction were separated out in a condenser. The aqueous layer was analyzed for its acetic acid content by titration with a 0.1 N solution of NaOH in the presence of phenolphthalein, and for acetone by the oxime method in the presence of bromophenol blue. The gas was analyzed by the usual method in the apparatus of the All-Union Thermo Technical Institute, the isobutylene being determined by absorption with 68% sulfuric acid. After each experiment, the catalyst was regenerated by passing air through at 600°.

In preliminary experiments, it was found that in the absence of a catalyst, at 300° and with contact times of 20 and 40 seconds, mesityl oxide did not undergo any change, regardless of whether it was passed through with or without water. During the passage of dry mesityl oxide over the aluminosilicate catalyst at 300°, a splitting of the mesityl oxide took place. The products of reaction, separated out in a condenser, were collected in the receiver; they formed two layers. The lower layer was a concentrated aqueous solution of acetic acid.

The data for a characteristic experiment, as given below, illustrate the results:

Experiment No. 9

Quantity of catalyst	30 ml
Duration of experiment	2 hours
Speed at which mesityl oxide passed . .	220 gm/l/hr.
Temperature	300°
Yield of acetic acid	31.2 mol. %
Yield of gas	23.4 mol. %
Composition of gas: CO ₂ C ₃ H ₆ CO H ₂ CH ₄	
8.8 22.9 12 19.1 48%	

Isobutylene content of olefins..... 70%

We must note that the mass of carbon distributed on the surface of the catalyst amounted to about 10% of the weight of mesityl oxide passed through. The dependence of the conversion of the mesityl oxide upon the steam:mesityl oxide ratio is given in Table 1 and Fig. 1.

It can be seen that at a temperature of 300° and a speed of passage of about 200 g per liter of catalyst per hour, the conversion of the mesityl oxide

increases with an increase of the steam: mesityl oxide ratio. The yield of acetic acid upon passage of the mesityl oxide likewise increases but the curve for the increase of the acetic acid yield has a maximum at the initial molar ratio of water: mesityl oxide of 5.7. At this point, the yield of acetic acid amounts to 65 molar %, that is, for 100 moles of mesityl oxide passed through, 65 moles of acetic acid are formed. With a 14.5-fold excess of steam, the yield of acetic acid consists of only about 50 mol. %.

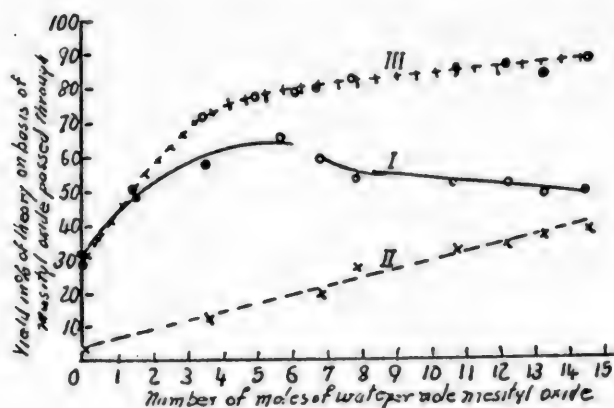


Fig. 1. Curve for dependence of conversion of mesityl oxide upon amount of steam.

I- Yield of acetic acid, II-yield of acetone, III-percent conversion of mesityl oxide

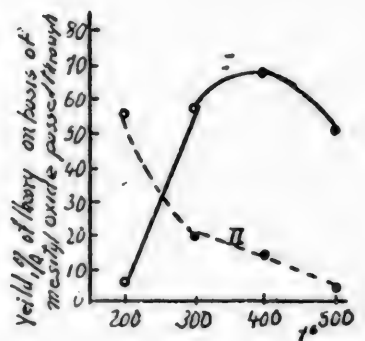


Fig. 2. Curve showing dependence of conversion of mesityl oxide upon temperature.

I-yield of acetic acid, II-yield of acetone.

Table 1

Catalytic Cracking of Mesityl Oxide on Aluminosilicate Catalyst in the Presence of Water Vapor
Volume of Catalyst layer 30 ml.

Temp. in °	molar ratio of water: mesityl oxide	speed of mesityl oxide (in gm/l of catalyst per hr.)	acetic acid obt. (in mole % based on mesityl oxide passed through)	Ratio of moles of gas obtained to moles of acid	acetone obtained (in mole % based on mesityl oxide passed through)	% of conversion of mesityl oxide to acetic acid and acetone	recovery of mesityl oxide (in % of mesityl oxide passed through)	Composition of the gas (in volume %)					
								CO ₂	C ₂ H ₂ n	CO	H ₂	CH ₄	isobutylene content of olefins
300	1.5	210	49.7	0.51			21.1						
300	1.6	230	51.1	0.46			23.6	7.8	63.6	1.2			
300	3.5	243	58.9	0.78	26.4	72.1	4.7	1.6	62.0	0.0	6.5	9.7	88.7
306	5	186	56.4	0.67	42.0	77.4	3.9	7.2	59.2	1.7			94.1
300	5.7	162	65.0	0.68			4.9	6.8	77.5	0.0	5.2	5.9	96.8
300	6.8	225	58	0.77	40.0	78.0	7.9	0.0	78.4	0.6			94.0
306	7	238	53.0	0.69	43.0	74.5	9.6	7.9		1.8	4	2.6	100
300	7.8	217	53.0	0.69	59.0	82.5		4.6	82.5	0.6	8.8	8.7	97
300	10.6	182	53.4	0.7	62.4	84.6	4.4	2.7	90.0	0.6	-	-	96.5
300	12.2	175	51.7	0.82	66.2	84.8	8.5	1.5	97.8	0.0	-	-	98.2
300	14.5	164	49.7	0.7	78.8	89.1	6.2	3.0	96.6	0.0	-	-	98.0

It is of interest that with an increased steam:mesityl oxide ratio, the yield of acetone grows continuously. Thus, with an initial steam:mesityl oxide ratio of 3, the yield of acetone is 22 mol.%, (i.e., 11% of the mesityl oxide is converted into acetone); with a steam:mesityl oxide ratio of 14.5, the yield reaches 78.8 mol %. In other words, 39.4% of the mesityl oxide is reconverted to acetone, and 49.7% split into ketene and isobutylene.

The greater the initial ratio of water:mesityl oxide, the greater the olefin content in the gaseous products of reaction, i.e., the less the usual products of cracking and polymerization. With a 12-fold volume of water, the content of olefins in the gas amounted to 96-98%, and of this, 98% was isobutylene.

Thus, under laboratory conditions, a completely pure isobutylene (after removal of the CO₂ mixed with it) can be obtained from acetone, diacetone alcohol, or mesityl oxide.

The ratio between the splitting reaction of mesityl oxide to give acetic acid and ketene, and the hydration reaction of mesityl oxide followed by splitting into acetone, depends to a great degree upon the temperature. This dependence is illustrated by the curve in Fig. 2, which refers to the series of experiments with an initial water: mesityl oxide ratio of 7.

At a temperature of 200°, 6.8% of the mesityl oxide is converted into acetic acid and isobutylene, 56% into acetone; at 400°, the reverse picture is observed: 68.7% is converted into acetic acid and 14.9% into acetone. At 500°, the yield of acetic acid falls to 50.5%, and the conversion into acetone to 4.4%.

SUMMARY

1. A study has been made of the catalytic decomposition of mesityl oxide into ketene and isobutylene in the presence of steam and aluminosilicate catalyst.
2. It has been shown that the yields of acetic acid and isobutylene vary, depending on the ratio of the amount of water to mesityl oxide. The maximum conversion of mesityl oxide into acetic acid at 300° is 65% after a single passage with a ratio of water to mesityl oxide of 5.7.
3. Simultaneously with the splitting of the mesityl oxide, there also takes place the formation of acetone from mesityl oxide and water, its extent depending upon the water: mesityl oxide ratio and upon the temperature.
4. The results obtained confirm the conclusion that the formation of acetic acid from acetone over oxide and aluminosilicate catalysts is the result of consecutive reactions: the condensation of acetone, and the subsequent splitting of the mesityl oxide.

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Received March 4, 1948.

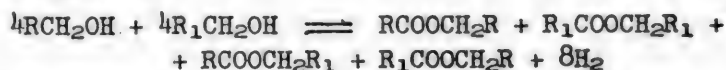
THERMODYNAMICS OF THE DEHYDRATION OF ALCOHOLS

THE EQUILIBRIUM OF THE REACTION: $2C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + 2H_2$

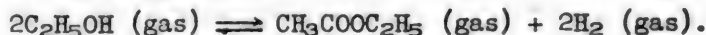
A. A. Vvedensky, P. Ya. Ivannikov and V. A. Nekrasova

Leningrad Institute of High Pressures

The reaction we have investigated is a partial example of the reaction of non-acid catalytic esterification of primary alcohols, taking place according to the general equation:



The literature contains only two works on the determination of the equilibrium constant for the esterification reaction of methyl alcohol [1]. There is no information in the literature on the determination of the equilibrium constant for the esterification of other alcohols. In our case, the reaction is expressed by the equation:



The experiments were performed in apparatus of a circulatory type, consisting of: 1) a metering device, permitting small, equal portions of reacting material to contact the catalyst; 2) a catalyst chamber, filled with catalyst; 3) a device for collecting the reaction products.

By this means, there was passed through the apparatus, with a very small volume speed at temperatures from 181-201.5°, ethyl alcohol or a mixture of ethyl alcohol with ethyl acetate and hydrogen. At the temperatures indicated, side reactions were very weakly expressed, and the separated gas consisted of pure hydrogen.

The ethyl alcohol and ethyl acetate used by us had the following constants: (Table 1).

Table 1

Substance	$n_D^{19.5}$	n_D^{20}	d_{20}^{20}	B.p. (°)
Ethyl alcohol .	1.36145	—	0.7956	78.3-78.4
Ethyl acetate .	—	1.3719	0.8983	77.2-77.4

In the liquid catalyzate, the condensate, obtained as a result of the experiment, the ethyl acetate, acetaldehyde, and acetic acid contents were determined. The amount of alcohol was determined by difference.

The gas formed was analyzed for CO_2 , unsaturates, O_2 , CO , H_2 , saturated hydrocarbons, and N_2 .

For the determination of the equilibrium constants of the reaction, experiments were conducted both from the side of dehydration of the ethyl alcohol, as well as from the side of hydration of the ethyl acetate. Then, in the final experiments, we passed through alcohol-ester mixtures which were close to the equilibrium composition, as determined by the preliminary experiments.

Table 2

Experimental data on the esterification of Ethyl Alcohol

Expt. No.	Temp. of expt. (°)	Direction of approach to equilibrium alcohol + ester -	Substance passed through	Ml H ₂ collected per g condensate	Composition of condensate (in weight %)			
					Ethyl acetate	Ethyl alcohol	Acetaldehyde	Acetic acid
1	181	+	C ₂ H ₅ OH	289	53.4	44.9	1.4	0.3
2	181	+	77% ester + 23% alcohol +	165	77.7	21.4	0.3	0.6
3	181	±	+ hydrogen	178	76.9	22.2	0.3	0.6
4	181	±	same	111	79.5	19.4	0.3	0.8
5	181	±	same	212	74.2	24.9	0.3	0.6
6	181	-	same	329	72.7	26.4	0.4	0.5
7	181	+	C ₂ H ₅ OH	292.5	52.3	46.4	0.6	0.7
8	201.5	±	See expts.	227	77.3	21.0	0.9	0.8
9	201.5	-	2-6	314	71.8	26.7	0.8	0.7
10	181	+	C ₂ H ₅ OH	not det.	52.0	not determined		

A summary of our experimental data is given in Table 2.

Experiments 1, 7, 10 (Table 2) are given to show that the activity of the catalyst was practically unchanged in the course of the entire series of experiments.

In Table 3 are given the data necessary for the calculation of equilibrium constants on the basis of the experiments, as well as the results of the calculation.

Table 3

Results of the calculation of equilibrium constants for the esterification reaction of ethyl alcohol

No. of Expt.	Temp. of expt. in °	atm. press. in mm.	Reaction products in mixture, expressed in moles						K _p
			ester n ₁	alcohol n ₂	hydrogen n ₃	aldehyde n ₄	acid n ₅	Σ n̄	
1	181	763	0.01650	0.02730	0.0350	0.000849	0.000137	0.07979	0.34
2	181	755.3	0.02622	0.01226	0.01446	0.00023	0.000406	0.05357	0.68
3	151	755.5	0.01651	0.00867	0.01380	0.000119	0.000201	0.03393	1.05
4	181	760.2	0.01985	0.01093	0.01800	0.000163	0.000224	0.04920	1.10
5	181	760.2	0.02312	0.01477	0.02598	0.000170	0.000280	0.06432	1.13
6	181	758.6	0.01746	0.01213	0.03101	0.000173	0.000180	0.06095	1.88
7	181	759.7	0.01442	0.02458	0.03164	0.000360	0.000290	0.07129	0.335
8	201.5	757.1	0.02134	0.01130	0.02466	0.000520	0.000310	0.05838	1.72
9	201.5	759.1	0.01926	0.01366	0.03305	0.000430	0.000290	0.06669	1.69

The values of the equilibrium constants given in Table 3 were calculated in the following manner:

$$K_p = \frac{p_{\text{CH}_3\text{COOC}_2\text{H}_5} \cdot p_{\text{H}_2}^2}{p_{\text{C}_2\text{H}_5\text{OH}}^2},$$

where:

$$P_{\text{CH}_3\text{COOC}_2\text{H}_5} = \frac{P_{\text{mm}}}{760} \cdot \frac{n_1}{\sum n};$$

$$P_{\text{H}_2} = \frac{P_{\text{mm}}}{760} \cdot \frac{n_3}{\sum n};$$

$$\text{and } P_{\text{C}_2\text{H}_5\text{OH}} = \frac{P_{\text{mm}}}{760} \cdot \frac{n_2}{\sum n}.$$

Recalling that $\sum n = n_1 + n_2 + n_3 + n_4 + n_5$, and substituting for the magnitude used in the equation, we obtain:

$$K_p = \frac{n_1 n_3^2}{n_2^2 \sum n} \cdot \frac{P_{\text{mm}}}{760}$$

An analysis of the data given in Table 3 shows that the most probable values of the equilibrium constant lie, for a temperature of 181°, in the interval 1.10-1.05, and for a temperature of 201.5°, in the interval 1.69-1.72. Therefore, for further calculations, we assumed that at 181° $K_p = 1.075$ and at 201.5° $K_p = 1.705$.

Evaluation of Results

To determine the dependence upon the temperature of the equilibrium constants of the reaction $2\text{C}_2\text{H}_5\text{OH} (\text{gas}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 (\text{gas}) + 2\text{H}_2 (\text{gas})$, we shall take on the basis of our experimental data the average values of K_p for the temperatures 181° and 201.5° equal to 1.075 and 1.705 respectively.

Accordingly, at:

$$\begin{array}{llll} t^\circ = 181, & T^\circ\text{K} = 454, & K_p = 1.075, & \lg K_p = 0.03141, \\ t^\circ = 201.5, & T^\circ\text{K} = 474.5, & K_p = 1.705, & \lg K_p = 0.23172. \end{array}$$

Whence we find:

$$\Delta H = \frac{4.57 \lg \frac{K_2}{K_1} T_2 \cdot T_1}{T_2 - T_1} = 9.620 \text{ cal.}$$

To the first approximation we may assume that the dependence of K_p on the temperature is expressed by the equation:

$$\lg K_p = \frac{-\Delta H}{4.57} + B. \quad (1)$$

Replacing in equation (1) ΔH by the value found, 9620 cal, and using the value of $\lg K_p$ calculated from experimental results (for example, at 454°K $\lg K_p = 0.03141$) we find that:

$$B = \lg K_p + \frac{\Delta H}{4.57 T} = 0.03141 + \frac{9620}{4.57 \cdot 454} = 4.66;$$

consequently:

$$\lg K_p = -\frac{9620}{4.57 T} + 4.66. \quad (1-a)$$

A more accurate equation for the dependence of $\lg K_p$ upon the temperature will be developed later.

Let us take for the specific heats:

$$\text{hydrogen: } C_p = 6.744 + 0.0002774T + 0.0_{\text{e}}1956 T^2 \quad (2)$$

$$\text{ethylacetate: } C_p = 2.27 + 0.88T - 0.0_{\text{4}}3086 T^2, \quad (3)$$

$$\text{Ethyl alcohol: } C_p = 5.5656 + 0.04522 T - 0.0_{\text{4}}1639 T^2 \quad (4)$$

Equation (2) has been calculated by us according to the data given in the paper of Wagmann, Kilpatrick, Taylor, Pitzer, and Rossini [2]. Equation (3) has been calculated by the method of Benewitz and Rosner [3], Equation (4) by the method of least squares from spectroscopic data given in the work of Brickweed, Moskow, and Aston [4].

Table 4
Comparison of the heat capacities of hydrogen, ethyl acetate, and ethyl alcohol, calculated according to the equations given above, with experimental data in cal/degree molecule (for gases)

Hydrogen			Ethyl Alcohol		Ethyl Acetate		
T°K	C _p		C _p		T°K	C _p	
	Exptl.	Calc.	Exptl.	Calc.		Exptl.	Calc.
300	6.895	6.845	17.66	17.66	346	29.7	29.0
400	6.974	6.886	21.00	21.03	385	32.7	31.6
500	6.993	6.932	24.09	24.08	410	33.7	33.2
600	7.008	6.981	26.81	26.80	440	35.3	35.0
700	7.035	7.034	29.18	29.19	—	—	—

A comparison of the numerical values of the heat capacity, calculated by means of these equations, with the experimental values, shows a satisfactory agreement, as is obvious from Table 4.

Combining equations (2), (3) and (4), we obtain for our reaction:

$$\Delta C_p = 4.627 - 0.0018852 T + 0.0000023112 T^2, \quad (5)$$

whence it follows that:

$$\Delta H_T = \Delta H_0 + 4.627 T - 0.0009426 T^2 + 0.087704 T^3$$

and

$$\Delta H_0 = \Delta H_T - 4.627 T + 0.0009426 T^2 - 0.087704 T^3,$$

at T = 464.3 (average temperature of our experiments):

$$\frac{474.5 + 454}{2} = 464.3;$$

$\Delta H_{464.3} = 9620$ cal, then:

$$\Delta H_0 = 9620 - 4.627 \cdot 464.3 + 0.0009426 \cdot 464.3^2 - 0.087704 \cdot 464.3^3 = 7663 \quad (6)$$

$$\Delta H_{298} = 7663 + 4.627 \cdot 464.3 - 0.0009426 \cdot 464.3^2 + 0.087704 \cdot 464.3^3 = 9063. \quad (7)$$

Now we can express the dependence of $\lg K_p$ upon the temperature by the following more accurate equation:

$$\lg K_p = \frac{-7663}{4.573 T} + \frac{4.627}{1.986} \lg T - 0.0002061 T + 0.0784 T^2 + C \quad (8)$$

Taking into account the values of K_p found by us experimentally, at T = 454 and 474.5 (0.03141 and 0.23172), we find that "C" at these temperatures will be equal respectively to -2.3923 and -2.3935; the average value of "C" is -2.3929, and thus, finally:

$$\lg K_p = \frac{1675.7}{T} + 2.33 \lg T - 0.0002061 T + 0.0784 T^2 - 2.3929. \quad (8-a)$$

A comparison of $\lg K_p$, calculated according to equations (8-a) and (1-a), with experimental values, is given in Table 5.

Table 5

Comparison of $\lg K_p$, calculated according to equations (1-a) and (8-a), with experimental data

t°	T°K	$\lg K_p$		
		(1-a)	(8-a)	Exptl.
25	298	-2.304	-2.305	-
127	400	-0.603	-0.588	-
181	454	0.024	0.0305	0.0314
201.5	474.5	0.224	0.2276	0.2317
227	500	0.450	0.4623	-

We can now determine the entropy of ethyl acetate, the heat of formation, and the free energy of its formation from its elements under standard conditions.

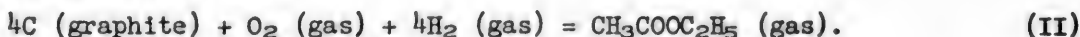
We found above from our experimental data for the reaction:



Taking as the value of the heat of formation of ethyl alcohol vapor from the elements:

$$\Delta H_{298} = -56240,$$

we find for the reaction:



$$\Delta H_{298} = -2 \cdot 56240 + 9036 = -103444.$$

To determine ΔF at a temperature of 298°K we shall take the value:

$$\lg K_p = -2.305 \text{ (Table 5). Then we have:}$$

$$\Delta F_T = -RT \lg K_p = -4.573 \cdot 298 \cdot (-2.305) = +3185.$$

Knowing the entropy of hydrogen and of ethyl alcohol:

$$\text{for hydrogen } S_{298}^\circ = 31.21 [5],$$

$$\text{for ethyl alcohol } S_{298.16}^\circ = 66.45 [4],$$

we find the entropy of ethyl acetate from the equation:

$$\Delta F_T = \Delta H_T - T \Delta S,$$

from which:

$$TS_{\text{ethyl acetate}} = \Delta H_T - \Delta F_T - 2TS_{H_2} + 2TS_{\text{alcohol}} = 26854$$

$$S_{\text{ethyl acetate}}^\circ = 90.11.$$

Now taking for:

$$C \text{ (graphite)} S_{298}^\circ = 1.367 [4]$$

and

$$\text{for oxygen } S_{298}^\circ = 49.00 [4],$$

we determine F_{298} for reaction (II) for the formation of ethyl acetate from the elements:

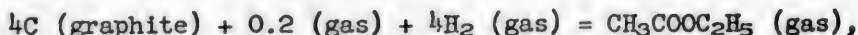
$$\Delta F_T = \Delta H_T - T \Delta S,$$

whence:

$$\Delta F_{298} = -76860.$$

Thus, corresponding to our experimental data:

1) The heat of formation and the free energy of formation of ethyl acetate from the elements:



$$\Delta H_{298} = -103444$$

and

$$\Delta F_{298} = -76860;$$

2) The entropy of ethyl acetate:

$$S_{298}^0 = 90.11.$$

We must note that the entropy of ethyl acetate, according to the data of Parks and Hoffman [8], differs from the value found by us. If we take the entropy indicated by them: $S_{298}^0 = 62.0$, and recalculate it to standard conditions, we find:

$$S_{298}^0 = 62.0 + \frac{8697}{298} + 4.573 \lg \frac{94.5}{760} = 62.0 + 29.2 - 4.13 = 87.07,$$

where 8697 is the latent heat of evaporation [7], and 94.5 is the vapor pressure of ethyl acetate at room temperature [8].

This value for the entropy leads to results differing from our experimental data, as is evident from what follows:

Let us take for our reaction:

$$\Delta H_{298} = 9036 \text{ cal}; \quad (7)$$

then

$$\Delta F_{298} = 9036 - T \Delta S.$$

Taking for:

$$\text{ethyl alcohol: } S_{298}^0 = 66.45 [+],$$

$$\text{ethyl acetate: } S_{298}^0 = 87.07,$$

$$\text{hydrogen: } S_{298}^0 = 31.21 [s];$$

we obtain for ΔF_{298} :

$$\Delta F_{298} = 9036 - 298(87.07 + 2 \cdot 31.21 - 2 \cdot 66.45) = 4092.$$

From this, utilizing the equation $\Delta F_T = -RT \lg K_p$, we find that at $298^\circ K$ $\lg K_p = \frac{4092}{4.573 T} = -2.98$, as against 2.3 (Table 4) calculated on the basis of our experiments at 454° and $474.5^\circ K$. If now, from equation (8):

$$\lg K_p = -\frac{1675.7}{T} + 2.33 \lg T - 0.0002061 T + 0.0784 T^2 + C,$$

we determine "C", taking the value of $\lg K_p = -2.98$ and then in order to find the dependence of the value of $\lg K_p$ upon the temperature, we obtain:

$$\lg K_p = -\frac{1675.7}{T} + 2.33 \lg T - 0.0002061 T + 0.0784 T^2 - 3.0688,$$

then:

$$\text{at } 454^\circ K: \lg K_p = -0.6454$$

$$\text{at } 474.5^\circ K: \lg K_p = -0.444.$$

Thus, the differences between our data and the data resulting from a value for the entropy of ethyl acetate equal to 87.07, are expressed in the following: see data in Table 6.

Table 6

Calc. No.	Magnitudes	According to data of Parks and Hoffman	According to our data
1	Entropy of ethyl acetate S_{298}^0	87.07	90.11
2	a): $\lg K_p$ b): K_p of reaction $2C_2H_5OH (gas) \rightleftharpoons CH_3COOC_2H_5 (gas) + 2H_2 (gas)$ and c) % ethyl acetate in condensate at:		
	(a)	- 2.98	- 2.3
	298°K (b)	0.001	0.005
	(c)	11.5	18.7
	(a)	- 0.6454	0.0314
	454°K (b)	0.2263	1.075
	(c)	50.0	66.3
	(a)	- 0.444	0.2317
	474.5°K..... (b)	0.3598	1.705
	(c)	55.1	70.9

SUMMARY

1. The equilibrium constants of the reaction $2C_2H_5OH (gas) \rightleftharpoons CH_3COOC_2H_5 (gas) + 2H_2 (gas)$ have been measured at 181 and 201.5°
2. An equation has been given to show the dependence of the logarithm of the equilibrium constant of the given reaction upon the temperature.
3. The heat of formation and the free energy of formation of ethyl acetate from its elements under standard conditions has been calculated.

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Received March 29, 1948.

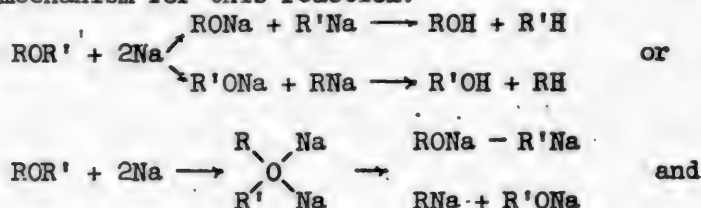
THE CLEAVAGE OF SIMPLE ETHER BONDS BY METALLIC SODIUM IN LIQUID AMMONIA

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In 1923 P.P. Shorygin [1] discovered a reaction for cleaving simple ethers by means of metallic sodium.

The reaction takes place upon heating the ethers with sodium: the high-boiling in open vessels, the low-boiling in sealed tubes. P.P. Shorygin proposed the following mechanism for this reaction.



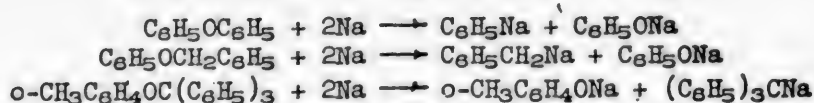
In the general case, 2 hydrocarbons and 2 hydroxyl derivatives are formed. Somewhat later, Ziegler and Thilman [2] found that several ethers with weakened bonds between the oxygen and carbon were easily cleaved even in the cold by liquid alloys of K and Na. These authors confirmed the mechanism of reaction suggested by P.P. Shorygin, assuming that the metal was introduced between the R and the OR in the compounds ROR. There is scarcely any initial dissociation of the ethers in accordance with the scheme: $\text{ROR}' \rightleftharpoons \text{R} + \text{OR}'$, as a result of which the radicals might react with sodium.

Schlenk and Bergmann [3] cleaved simple ethers with powdered sodium, obtained by dispersing the sodium in toluene. Later, P.P. Shorygin and Skoblinskaya [4] utilized a solution of sodium in liquid ammonia to split simple ethers. It appeared that the cleaving action of such solutions was far greater than that of the alloyed metals. Simple ethers were cleaved by solutions of metallic sodium or potassium in the cold, at -33° (the boiling point of liquid ammonia).

However, not all the simple ethers are cleaved by the metals and their solutions with equal ease. The ease of cleavage depends on the nature of the radical. P.P. Shorygin showed that aromatic ethers and the aromatic ethers of aromatic alcohols were cleaved by metallic sodium with especial ease. The ethers of the aliphatic series were cleaved with great difficulty. According to the results of P.P. Shorygin and S.A. Skoblinskaya [4], diphenyl, phenyl-benzyl, and o-tolyltriphenylmethyl ethers are easily cleaved by a solution of metallic sodium in liquid ammonia.

The theoretical quantity of metallic sodium (2 atoms per molecule of ether) reacting for from 5 to 7 days results in approximately 50% cleavage of these ethers. If a great excess of metallic sodium is used, and the reaction is carried out with mechanical stirring, these ethers are quantitatively cleaved. The cleavage takes place in only one direction:

* Data obtained by S. A. Skoblinskaya and here published for the first time.



Earlier, P.P. Shorygin [5,6] found that in the case of benzyl and o-tolyl triphenylmethyl ethers, there took place during the heating with metallic sodium what he called carbinol and phenol rearrangements. No signs of these rearrangements were observed when the reactions were carried out in the cold with a solution of metallic sodium in liquid ammonia.

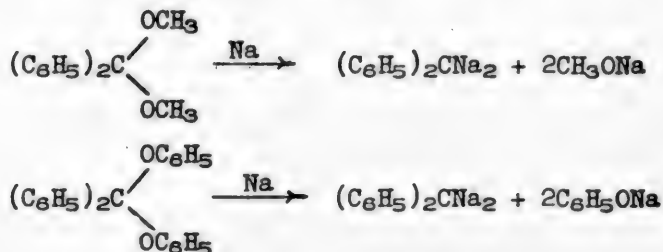
Sartoretto and Sova [7] studied the direction of the cleavage of substituted diphenyl ethers by metallic sodium in liquid ammonia as affected by the character and position of the substituents in the benzene nucleus. The authors showed that in monosubstituted diphenyl ethers, the bond between the benzene ring and the oxygen atom was strengthened by the substituents: o-CH₃, p-CH₃, p-OCH₃, o-NH₂, p-NH₂, arranged in the order of their increasing activity. The bonds with the O atoms were weakened by the substituents: o-OCH₃, o-COONa, p-COONa, also in the order of their increasing activity.

Thus, for example, the phenyl ether of p-carboxyphenol gave upon cleavage 100% phenol and 100% benzoic acid. The cleavage of alkylarylethers by metallic sodium in liquid ammonia was more difficult than the cleavage of aromatic ethers. S.A. Skoblinskaya and P.P. Shorygin found that anisole was cleaved to the extent of only 23% even when a 20-fold excess of metallic sodium was used, and the reaction was carried out for 5 days with mechanical stirring. Under the same conditions, veratrole was cleaved 34%, giving guaiacol. In order to cleave alkyl-alkyl ethers like diethyl and diisooamyl, heating with metallic sodium up to 340° was necessary.

Shorygin and Skoblinskaya [4] found that solutions of metallic sodium in liquid ammonia also did not produce cleavage of these ethers. This had been earlier noted by Kraus [8], who had demonstrated that the ethers of the lower alcohols were stable to the action of sodium in liquid ammonia.

S.A. Skoblinskaya and P.P. Shorygin investigated the action of a solution of metallic sodium in liquid ammonia upon acetals and ketals.

Both the acetal groups were split off, the oxygen remaining bound to the alcohol radicals which had formed the acetals and ketals. Upon using a 20-fold excess of Na, the diphenyl ketal of benzophenone was 95% cleaved; the dimethyl ketal, 87%.

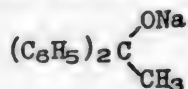


Wooster [9] found that during the action of two equivalents of Na upon one molecule, the reaction with the diethyl ketal of benzophenone in liquid NH₃ went chiefly according to the scheme:



According to the results of Ziegler [2], liquid alloys of K and Na split off only a single OCH₃ group from the dimethyl ketal of benzophenone. According

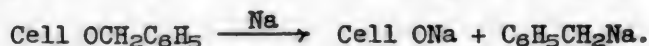
to the data of Schlenk and Bergmann [3]; powdered Na in ether behaved analogously; however, in this case, there was a rearrangement, as a result of which there was finally formed



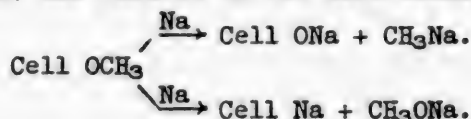
S.A. Skoblenskaya and P.P. Shorygin found that the diisoamyl acetals of benzaldehyde were 55% cleaved under the action of a 20-fold excess of sodium in liquid NH_3 for 5 days. Under these conditions, the diisoamyl acetal of oenanthic aldehyde was not cleaved.

The reaction with metallic Na in liquid NH_3 was applied to carbohydrate ethers by Shorygin and Makarova-Zemlyanskaya (Shorygina) [10]. They found that under the action of Na in liquid ammonia at 20° , trimethyl levoglucosan gave phenol in a yield of 34%. The reaction, obviously, is based upon the cleavage of simple ethers by sodium and metallo-organic compounds of sodium.

The simple ethers of cellulose are also cleaved by a solution of Na in liquid NH_3 . P.P. Shorygin and N.N. Makarova-Zemlyanskaya [11] showed that in the case of the benzyl ethers, the reaction took place only according to the equation:



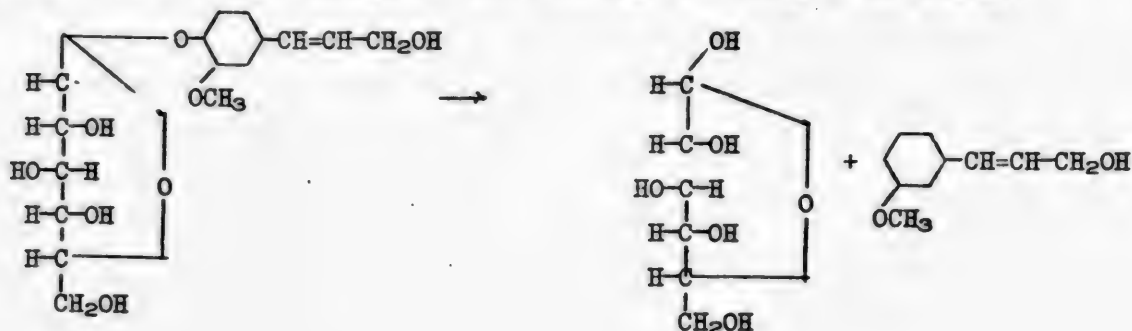
The methyl ether was cleaved in two directions:



According to the findings of N.N. Shorygina [12], α - and β -methylglucosides are not cleaved by solutions of metallic Na in liquid NH_3 , even under pressure at 20° . Freudenberg [13] showed that a solution of metallic K in liquid NH_3 also did not cleave methylglucosides. However, according to his results, the phenol glucoside was completely cleaved under these conditions, giving glucose. Other components of the cleavage mixture were not isolated.

We have investigated the action of a solution of Na in liquid NH_3 at -33° upon the glucosides: arbutin and coniferin.

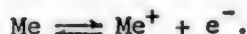
For the reaction, 20 g of Na and 5 g of glucoside were taken. This constitutes a great excess, as in order to react with all the free hydroxyl groups and a single ether bond, it would be necessary to take for 5 g of coniferin only 2.4 g of Na, and for 5 g of arbutin, 3.2 g of Na. The reaction took place over a period of 5 days. Under these conditions, arbutin did not appear to be cleaved. Under the same conditions, coniferin was partially cleaved, up to 10 or 12%. The cleavage took place fundamentally according to the scheme:



Simultaneously with this reaction, hydrogenation apparently takes place.

In order to explain the above-indicated facts about the lack of uniform behavior by various compounds with C-O-C bonds under the action of metallic Na, we must pay attention to the different properties of the oxygen atoms in these compounds.

In accordance with Kraus's [8] assumption, we shall assume for the present that alkaline metals dissolved in liquid NH₃ are dissociated into cations and electrons:



Upon dilution, the dissociation of the metal is accompanied by the association of molecules of ammonia with the electrons:

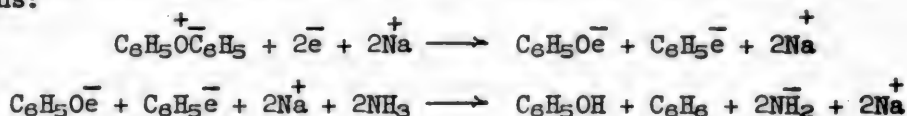


Thus, the active component of solutions of alkaline metals in liquid ammonia may be the electron.

The assumption that solutions of alkaline metals in liquid ammonia react because of the behavior of the electrons has been made recently by many investigators: with regard to the cleavage of phenyl ethers, by Sartoretto and Sova [7]; with regard to the hydrogenation of unsaturated hydrocarbons, by Huckel and Breitschneider [14]; with regard to hydrogenation in liquid NH₃, by Birch [15], and by others.

If we assume that the action of alkaline metals and their solutions is based on the giving up of electrons, then it is obvious that the latter will add on in those places where their density is least. The oxygen of dialkyl ethers has a pair of free electrons, and consequently, has no tendency to add new ones. In aromatic ethers, as for example, diphenyl ether, the ether oxygen atom has a positive charge in consequence of the electromeric effect, manifested in the presence of free electrons in the solution, and conditioned by the system of double bonds of the benzene ring.

Under the action of a solution of metallic sodium in liquid ammonia or of an alkaline metal alloy, the oxygen atom of such ethers will attract electrons. The cleavage of diphenyl ether by Na in liquid NH₃ may be formulated, in accordance with the assumptions of Kraus and Sartoretto and Sova, as in the following equations:



Alkylaryl ethers have the tendency to cleave both under the action of an alkaline, as well as of acid reagents.

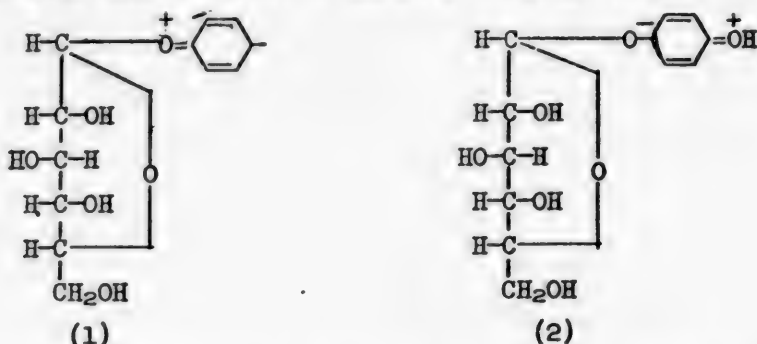
Under the action of alkaline metals and their solutions, the reaction, however, goes only in the direction:



Alkyl glucosides are not cleaved by solutions of alkaline metals, just as alkylalkyl ethers are not, because of the absence of the electromeric effect.

The cleavage of phenyl glucoside, observed by Freudenberg, may also be explained by the attraction of electrons away from the oxygen atom by the benzene ring (1).

It is obvious that the presence of the phenol group in the para position to the glucoside bond in arbutin inhibits cleavage (2):



The glucoside coniferin, splitting under analogous conditions only partially, also possesses several electromeric effects. However, the condition of the molecule is complicated by the presence of a methoxyl group in the nucleus, of a double bond conjugated with the nucleus, which has a tendency to be hydrogenated under the given conditions, and of a hydroxyl group in a side chain.

EXPERIMENTAL

Action of a Solution of Metallic Na in Liquid NH_3 Upon Arbutin

A 4.8 g portion of arbutin was dissolved in 400 ml of liquid NH_3 . To this was then added 20 g of metallic Na. The reaction was allowed to continue for 5 days. After removal of the ammonia and subsequent displacement of the residue by a current of dry nitrogen, moist ether was added to the reaction mixture. The alcoholic alkaline solution was neutralized, and then acidified with carbonic acid and extracted with ether in order to remove the phenolic products of the cleavage. After driving off the ether from the latter, there remained only negligible traces of a dark syrupy material. The aqueous residue was again accurately neutralized with alkali, evaporated to dryness, and the residue extracted with absolute alcohol.

From the alcoholic solution there was obtained 4.3 g of a substance which melted, after recrystallization from alcohol, at 188° , and gave no depression in a mixed melting point test with the initial arbutin.

Action of a solution of Na in Liquid NH_3 Upon Coniferin

The conditions of the reaction were similar to those utilized for arbutin. After accurate neutralization of the alkaline water-alcohol solution with sulfuric acid, the solution was extracted with ether. The ether extract was dried, and the ether driven off. There remained 1 g of a syrupy material which appeared to be a glucoside, in view of the fact that the action of emulsin for 7 days at 30° gave 0.495 g of glucose. The quantity of the latter was determined by Bertrand's method. This quantity corresponded to 0.946 g of coniferin, or 18.9% of the original 5 g. The glucoside was apparently a product of the hydrogenation of coniferin. It gave a benzoate by the Schotten-Bauman reaction, with a melting point of $140\text{--}150^\circ$.

After the extraction with ether, the neutral water-alcohol solution was acidified with a current of CO_2 , and then extracted with ether. This ether extract gave insignificant traces of a syrupy dark substance. This indicates that phenol was not formed during the cleavage.

*This was poured off the solid residue on the following day. Alcohol was then added to the reaction mixture.

The remaining aqueous solution was evaporated and the residue extracted with absolute alcohol. After the alcohol was driven off, 3.15 g of a solid substance was obtained. The product had reducing properties corresponding to 0.281 g of glucose, determined by Bertrands method. This corresponded to 0.535 g of coniferin, or 10.7% of the original 5 g. Thus, it appeared that 10.7% of the coniferin was cleaved by Na in liquid NH_3 in the direction of glucose formation. The total quantity of glucoside separated from the aqueous solution was equal to $3.15 - 0.535 = 2.615$ g, or 52.3% of the original 5 g. The total quantity of glucoside recovered from the reaction without cleavage was:

$$52.3\% + 18.9\% = 71.2\%.$$

SUMMARY

1. Alkyl glucosides, as well as dialkyl ethers and acetals of the aliphatic series, are not cleaved by solutions of alkaline metal in liquid ammonia. This is explained by the absence of a tendency in the ether oxygen of these compounds to add electrons.

2. Aryl ethers, aromatic acetals and ketals are easily cleaved by sodium in liquid ammonia. In consequence of the electromeric effect, these compounds tend to add electrons.

3. The differences in behavior of substituted phenol glucosides toward a solution of Na in liquid ammonia is explained by the influence of the substituents upon the glucoside oxygen.

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Received February 23, 1948.

THE PREPARATION OF SALTS OF ALIPHATIC ACIDS.: I

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There is a very extensive literature which refers to the salts of aliphatic and naphthenic acids; most of the references in this field, as is natural, refer to the salts of sodium and potassium, while the salts with other cations have been studied to a much lesser degree.

The incompleteness of the literature and the practical value of salts of aliphatic and naphthenic acids applied to power engineering, medicine, the production of construction materials and water-impermeable fabrics, the lacquer color industry, and so on, stimulated us to make a study of several salts of aliphatic and naphthenic acids. In our first communication, we present the results of an investigation of salts of bismuth and antimony.

A patent of Hoffman [1] gives the following method of obtaining bismuth oleate: to an alcoholic solution of sodium oleate, bismuth nitrate is added in a 13% solution of mannitol. Bismuth oleate precipitates out in the form of an anhydrous salt, completely insoluble in water, but soluble in ether, benzene, and other organic solvents.

M. Picon [2], who devoted considerable time to a study of bismuth salts of fatty acid, gives two methods for preparing them. The first is similar to that given in Hoffmann's patent, and consists in the reaction of the sodium salts of aliphatic acids with bismuth nitrate, dissolved in aqueous glycerine.* By this means, there are obtained basic salts of the general formula $(RCOO) \cdot BiO$ or $RCOO \cdot BiOH_2$. The basic salts are white or yellow powders, insoluble in naphtha and other organic solvents, with the exception of carbon disulfide.

The second method is the action of the aliphatic acid upon the yellow oxide of bismuth, Bi_2O_3 , during heating upon a water bath. By this method, the neutral salts $(RCOO)_3Bi$ are formed. These are also powders of a white or yellow color, but they differ from the basic salts by their solubility in naphtha, benzene, and other organic solvents, including olive oil.

The author, who has studied the conditions for the formation of bismuth salts of octylic and palmitic acids in detail, gives data for the analysis of the compounds obtained by him, but these are insufficiently accurate. Basic bismuth palmitate, formed as an admixture by the method of double decomposition in a glycerine medium, likewise did not possess a definite composition. In this paper, Picon gives the melting point of neutral bismuth palmitate as 82° .

In the work of Lauter, Jurst, and Christiansen [3], there are given the formulas and descriptions of the bismuth salts of aliphatic acids obtained by the authors according to Hoffmann's method. Bismuth oleate, $Bi(OH)_2 \cdot C_{18}H_{33}O_2$, was obtained in the form of a yellow powder, the stearate $Bi(C_{18}H_{35}O_2)_3$ and palmitate $Bi(C_{16}H_{31}O_2)_3$ were white powders.

In addition to these investigations, the literature contains a series of

* For the solubility of bismuth nitrate in aqueous glycerine see also I.G. Farbenindustrie, Zbl. 1937, II, 2713.

patents, referring chiefly to the solubility of bismuth oleate in various oils. The latter preparation has an important significance in medicine.

There are only two patents in the literature which refer to the preparation of antimony oleate. A patent of 1938 [4] gives two methods of obtaining antimony oleate:

1. The treatment of oleic acid by antimony trichloride in ethyl ether in the presence of diethylamine;
2. The action of Sb_2O_3 upon oleic acid at high temperature and removal of the water formed in vacuum.

A 1941 patent [5] gives a method for obtaining antimony oleate by treating sodium oleate with antimony trichloride in an anhydrous solvent, for example, ethyl ether, or olive oil. There are also references to the fact that antimony oleate is obtained in the form of a viscous oil, easily miscible with other oils. There are no other data in the literature.

EXPERIMENTAL

Bismuth Salts

We decided to utilize both methods of preparation of bismuth oleate.

1) 5.45 g of chemically pure oleic acid (Kahlbaum) was dissolved in 30 ml of ethyl alcohol, neutralized with 16.2 ml of a normal solution of caustic soda, and precipitated at room temperature by a solution of bismuth nitrate in aqueous glycerine: 3.5 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in a mixed solution of 10 g glycerine and 20 ml water. The white precipitate which separated out was immediately filtered off on a Buchner funnel, washed with water until there was no reaction for NO_3^- , the traces of oleic acid removed with ethyl alcohol, and the residue dried in a dessicator at 105° . The bismuth oleate obtained was a yellowish white oil of a salve-like consistency. The yield of salt was 4.9 g, or 72.38% of theory.

0.1484 g substance: 0.0388 g Bi_2O_3 .

0.1726 g substance: 0.0453 g Bi_2O_3 .

Found %: Bi_2O_3 26.17, 26.29; Bi 23.48, 23.58.

$\text{Bi}(\text{C}_{18}\text{H}_{33}\text{O}_2)_3$. Calculated %: Bi_2O_3 22.15; Bi 19.87.

Thus, the preparation was the neutral salt, slightly contaminated by the basic salt as impurity.

2) To 3 g of oleic acid were added 1.1 g of yellow oxide of bismuth in powdered form and 1 ml of distilled water. The mixture was heated on a water bath for 10 hours. The water formed in the reaction was removed by treating the mixture with carbon tetrachloride, and heating on the water bath until complete evaporation of the liquid. This was done three times. The mixture was then dissolved with gentle heating in carbon tetrachloride and filtered through a linen filter. After evaporation, the filtrate gave a yellow oily material that 1.78 g, or 47.85% of theory on the assumption that it was the neutral bismuth salt.

0.1060 g substance: 0.0262 g Bi_2O_3 .

Found %: Bi_2O_3 24.72; Bi 22.17

$\text{Bi}(\text{C}_{18}\text{H}_{33}\text{O}_2)_3$. Calculated %: Bi_2O_3 22.15; Bi 19.87.

The residue insoluble in CCl_4 was grayish-white; it was separated from the bismuth oxide that had not taken part in the reaction by shaking with carbon tetrachloride. The heavy Bi_2O_3 quickly precipitated in a day, and the cloudy solution was passed through a linen filter. A grayish-yellow oil remained on the filter; drying converted this into a powder, slightly greasy to the touch.

It weighed 1.86 g, 34.83% of theory on the assumption that it was the basic salt of bismuth.

0.1018 g substance: 0.0469 g Bi_2O_3 .

Found %: Bi_2O_3 46.06; Bi 41.32.

$\text{Bi}(\text{OH})_2(\text{C}_{18}\text{H}_{33}\text{O}_2)$. Calculated %: Bi_2O_3 44.46; Bi 39.82

Thus, by the first method, i.e., the double decomposition of sodium oleate and bismuth nitrate, the neutral salt of bismuth was obtained.

By the second method, i.e., the treatment of the yellow oxide of bismuth, Bi_2O_3 , with oleic acid, there were obtained almost equal portions of the neutral salt $\text{Bi}(\text{C}_{18}\text{H}_{33}\text{O}_2)_3$ and the basic $\text{Bi}(\text{OH})_2(\text{C}_{18}\text{H}_{33}\text{O}_2)$.

The two salts show sharp differences in their behavior to solvents. The neutral salt dissolved in benzene, carbon tetrachloride, and to some extent in ethyl alcohol. The basic salt is insoluble in every one of these solvents.

The results obtained by us differ from those of Picon, who had asserted that the reaction of sodium salts of aliphatic acids with bismuth nitrate in aqueous glycerine solution gave the basic salts. As our investigations have shown, this method gives the neutral salts with a small admixture of basic salts. It is possible that a slight change in the method of obtaining the bismuth oleate has influenced the results. Instead of heating for 20 hours, we continued our treatment for 10 hours, and instead of naphtha, we used carbon tetrachloride. The bismuth oleate we obtained was a greasy white or slightly yellow colored substance, in contrast to the findings of Picon and his coworkers, who described bismuth oleate as a yellowish powder.

Bismuth palmitate and stearate were obtained by the first method: the reaction of the sodium salts of the aliphatic acids with bismuth nitrate in aqueous-glycerine solution.

To obtain bismuth palmitate, we prepared two solutions:

1) 4.3 g of sodium palmitate (with a total alkalinity of 10.85) in 15 g of glycerine and 40 ml of water.

2) 2.8 g of bismuth nitrate in 10 g of glycerine and 20 ml of water.

The second solution was poured a little at a time into the first solution, with stirring and heating on a water bath. A white, dense, flocculent precipitate was filtered off on a Buchner funnel, washed carefully with water, and dried at a temperature of 80° . The bismuth palmitate was a yellowish white powder. The yield of salt was 5.12 g, or 93.94%.

0.1496 g substance: 0.0370 g Bi_2O_3 .

0.2100 g substance: 0.0512 g Bi_2O_3 .

Found %: Bi_2O_3 24.74, 24.32; Bi 22.14, 21.82.

$\text{Bi}(\text{C}_{16}\text{H}_{31}\text{O}_2)_3$. Calculated %: Bi_2O_3 23.92; Bi 21.49.

The bismuth palmitate showed good solubility in benzene and carbon tetrachloride, was partially soluble in ethyl alcohol, and weakly soluble in ethyl ether.

To obtain bismuth stearate, 3.5 g of sodium stearate (with total alkalinity 10.86) was dissolved in 10 g of glycerine and 20 g of water, and mixed with 2.5 g of bismuth nitrate in 7.5 g of glycerine and 15 g of water, while the solutions were stirred and heated on a water bath. The flocculent yellowish precipitate was filtered off on a Buchner funnel, and dried at 80° . It was a light grayish yellow powder. Yield 4.2 g, or 96.79%.

0.1112 g substance: 0.0296 g Bi_2O_3 .

0.1020 g substance: 0.0276 g Bi_2O_3 .

Found %: Bi_2O_3 26.61, 27.08; Bi 23.88, 24.29.

$\text{Bi}(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$. Calculated %: Bi_2O_3 22.02; Bi 19.75.

The preparation was the neutral bismuth salt $\text{Bi}(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$ mixed with some basic salt $\text{Bi}(\text{OH})_2(\text{C}_{18}\text{H}_{35}\text{O}_2)$.

The bismuth stearate dissolved well in benzene and carbon tetrachloride upon heating, and was rather weakly soluble in ethyl alcohol and ethyl ether.

In Table 1 are given the qualitative data with regard to the solubilities of the bismuth salts.

Table 1

Solubility of Bismuth Salts of Aliphatic Acids

Solvent	Bismuth oleate neutral salt	Bismuth oleate basic salt	Bismuth palmitate	Bismuth stearate
Water	Insoluble	Insoluble	Insoluble	Insoluble
Ethyl alcohol	Slightly soluble	Insoluble	Slightly soluble	Slightly soluble
Ethyl ether	Very slightly soluble	Insoluble	Barely soluble	Slightly soluble
Benzene	Dissolves upon heating	Insoluble	Dissolves upon heating	Dissolves upon heating
Carbon tetrachloride	Dissolves upon heating	Insoluble	Dissolves upon heating	Dissolves upon heating

Bismuth salts are utilized in medicine in the form of solutions or suspensions in vegetable oils. According to the data of Picon, the solubility of bismuth palmitate reaches 0.7 g per liter.

We have studied the solubility of bismuth salts in transformer oil, utilizing the usual method described by Ostwald-Luther.

Our investigations on the solubility of bismuth salts in transformer oil show that their solubility, despite the fact that it increases with a rise in temperature, is still not very great. In Table 2 are listed all the data we have obtained on the solubility of bismuth salts at 13, 30, and 70°. Only the neutral bismuth salts were investigated.

Table 2

Solubility of bismuth oleate, palmitate, and stearate in transformer oil (in g per 100 g of solvent)

Salt	13°	30°	70°	Note
Bismuth oleate	0	0.16	0.45	The solid phase in all cases was the unchanged salt.
Bismuth palmitate.....	Traces	0.31	0.84	
Bismuth stearate.....	0	0.45	0.72	

In conclusion, we studied the behavior of bismuth salts upon heating. As was to be expected, on the basis of the colloid nature of the aliphatic acid

salts, we found an extended melting range for the compounds. Results are given in Table 3.

Table 3

Melting Range of Bismuth Salts of Aliphatic Acids

Bismuth oleate - neutral salt	62-70°
Bismuth oleate - basic salt	76-80°
Bismuth palmitate - neutral salt.....	84-88°
Bismuth stearate - neutral salt	98-106°

Antimony Salts

Our investigations began with the attempt to obtain antimony oleate by treating sodium oleate with antimony trichloride. 5.3 g of chemically pure oleic acid (Kahlbaum) was mixed with 0.75 g of NaOH in methanol, with heating on a water bath. To remove the water formed by the reaction between the oleic acid and NaOH, the mixture was twice boiled with methanol to the point of complete dryness. The cooled residue was dissolved in ethyl ether and to the solution there was added little by little 1.2 g of SbCl_3 , also dissolved in ether. Upon the addition of SbCl_3 , the mixture boiled up very jerkily. When all the antimony trichloride had been added, the mixture was carefully boiled on a water bath for three hours. A fine white powder precipitated out of the solution and drops of a yellow oil separated out; these were oleic acid which had not entered into the reaction. The precipitate was filtered off and dried in a dessicator. The product was a rosy white fine powder, greasy to the touch. Yield 2.1 g, or 32%.

The analysis of the salt was carried out in the following manner: a sample of the salt was treated with 2 N HCl until it was completely decomposed. The antimony was precipitated with hydrogen sulfide and determined in the form of Sb_2S_3 .

0.1106 g substance: 0.0392 g Sb_2S_3 .

Found %: Sb 25.42.

$\text{SbO} \cdot (\text{C}_{18}\text{H}_{33}\text{O}_2)$. Calculated %: Sb 29.09.

Upon heating, the antimony oleate began to turn yellow at about 125°, meanwhile softening, and melting within the limits 136-142°. The behavior of antimony oleate with various solvents was also studied. Results are given in Table 4.

Antimony palmitate, prepared in the same manner, was a white powder.

0.1036 g substance: 0.0221 g Sb_2S_3 .

Found %: Sb 15.30.

$\text{Sb}(\text{C}_{16}\text{H}_{31}\text{O}_2)_3$. Calculated %: Sb 13.74.

Upon heating to 70°, antimony palmitate turns yellow; it melts at 84-88°. Upon further heating to 120°, it begins to boil, with decomposition. Its behavior with solvents is shown in Table 4.

Antimony stearate, prepared similarly, was a fine grayish-yellow powder.

0.1184 g substance: 0.0279 g Sb_2S_3 .

Found %: Sb 16.89.

$\text{Sb}(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$. Calculated %: Sb 12.55.

In table 4 are given qualitative data on the solubility of antimony stearate.

Upon heating to 96-98°, antimony stearate begins to soften; it melts within the limits of 100-106°.

Table 4
Solubility of Antimony Salts of Aliphatic Acids

Solvent	Antimony oleate	Antimony palmitate	Antimony stearate
Water	Insoluble, but decomposed	Decomposed by water upon heating	Decomposed upon heating
Ethyl alcohol	Weakly soluble, both cold and hot		
Benzene	Difficultly soluble both cold and hot	Weakly soluble	Weakly soluble
Carbon tetrachloride	Weakly soluble	Insignificantly soluble	Weakly soluble
Methyl alcohol		Easily soluble, especially upon heating	Soluble upon heating
Ethyl ether	Weakly soluble	Weakly soluble	Weakly soluble

By the other method of treatment, 5 g of oleic acid and 2 g of antimony oxide (Sb_2O_3) gave about 1 g of a heavy yellow semi-transparent liquid; in order to free it from the powdered Sb_2O_3 mixed with it, the mixture was treated with ethyl ether and filtered through a linen filter. Two layers were obtained; the lower was a light yellow transparent solution, the upper ether with dissolved oleic acid. The lower layer was separated from the ether in a separatory funnel, and dried in a dessicator. A total of 0.9 g of product was obtained. This was a light yellow liquid, which boiled within the limits $101-109^\circ$, and solidified at $4-5^\circ\text{C}$. This material was decomposed by water, forming a white, cloudy solution; it was also decomposed by hydrochloric acid; it was insoluble in ether; upon heating to dryness in glass, there remained a dull, greasy, yellowish-white stain. Upon heating to 140° , this substance showed no change; an aqueous solution gave a white, curdy precipitate of barium oleate with BaCl_2 . A drop reaction with phosphomolybdic acid showed the presence of antimony by the appearance of a characteristic blue spot. Hydrogen sulfide gave an orange precipitate of Sb_2S_3 . The substance dissolved fairly well, but not completely, in transformer oil.

0.1326 g substance: 0.0204 g Sb_2S_3 .

Found %: Sb 11.02.

$\text{Sb}(\text{C}_{18}\text{H}_{33}\text{O}_2)_3$. Calculated %: Sb 12.62.

Table 5
Solubility of Antimony Salts in Transformer Oil (in g per 100 g of oil)

Salt	12°	30°	70°	Note
Antimony oleate.....	0.96	6.2	—	The solid phase was the unchanged salt
Antimony palmitate	0.32	0.52	0.86	
Antimony stearate	0.10	0.32	—	

Thus, the substance was antimony oleate, apparently in the form of the neutral salt. We must note that the solid antimony salts contain sodium chloride impurity; the separation of the latter is especially difficult.

To obtain the palmitates and stearates, we used stearic acid with a melting

point of 68-70°, and palmitic acid with m.p. 62°.

We consider it a pleasant duty to express our thanks to V.A. Golubtsov, as a result of whose suggestion we carried out this research.

SUMMARY

1. Bismuth salts of oleic, palmitic, and stearic acids have been obtained.
2. Bismuth oleate was obtained in the form of neutral and basic salts; bismuth palmitate and stearate were obtained as neutral salts.
3. The melting ranges of all the bismuth salts obtained were determined; their behavior with various solvents and their solubility in transformer oil were also studied.
4. It was found that Picon's method gave the neutral salts with slight admixtures of the basic salts (instead of giving chiefly the basic salts, as Picon had asserted).
5. The antimony salts of oleic, palmitic, and stearic acids were obtained.
6. Neutral antimony oleate $\text{Sb}(\text{C}_{18}\text{H}_{33}\text{O}_2)_3$ is an oily liquid; the solid antimony oleate is the basic salt $\text{SbO}(\text{C}_{18}\text{H}_{33}\text{O}_2)$.
7. Antimony palmitate and stearate are neutral salts.
8. The melting range of all the forms of antimony salts obtained was determined; the behavior of the antimony salts in various solvents has been studied, as well as the solubility of antimony salts in transformer oil.

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Received January 13, 1948.

THE CHARACTERISTICS OF α,β -UNSATURATED KETONES.. IV

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α,β -unsaturated carbonyl compounds, including ketones, are characterized by many specific peculiarities, which distinguish them from the great mass of unsaturated compounds. It is to these that we owe the reduction of α,β -unsaturated ketones by nascent hydrogen, with the formation of saturated ketones, the hydration reaction under the influence of alkaline reagents, and the addition reactions of the elements of ammonia, hydrogen cyanide, and other compounds at the ethylene bond. The peculiarities of α,β -unsaturated ketones are shown also in their behavior toward Grignard reagents, which leads to the formation, in addition to that of tertiary alcohols, the normal products, of saturated ketones and other keto and diketo compounds.

Kohler [1] was the first to draw attention to the relation between the structure of α,β -unsaturated ketones and the course of the Grignard reaction, and showed that the normal course of reaction was favored by the presence in the ketones near the CO group of radicals having small volumes, and on the β -carbon atom of radicals with large volumes.

Later, Colonge [2], in investigating the course of the Grignard reaction as applied to α,β -unsaturated ketones, arrived at the following conclusions: the normal course of the reaction is influenced by the bond of the 1 carbon of

the conjugated system: $\overset{1}{\text{C}}=\overset{2}{\text{C}}-\overset{3}{\text{C}}=\overset{4}{\text{O}}$ with other radicals, thus confirming Kohler's conclusion. On the other hand, the presence of a radical upon carbon 2 and the absence of a radical upon carbon 1 hinders the normal course of the Grignard reaction. Finally, if carbons 1 and 2 both have radicals, the normal course of reaction is favored.

These conclusions show that the ideal of the mutual influence of the atoms in directing the reaction of a complicated molecule, put forward by V.V. Markovnikov [3], retains its significance as before.

Its correctness, confirmed by the authors named above on the basis of a constitutional factor, in view of the fact that this is only one of the factors determining the direction of the reaction, can not pretend to any universal validity, especially as it has been deduced on the basis of the study of only a single Grignard reaction, without taking into account the influence of the nature of the radicals.

It appeared to us that in order to decide the question of the special influences on the reaction, and the direction of the reaction in the case of α,β -unsaturated ketones, it would be expedient to make a fundamental study of the conjugation of the double bonds.. On the basis of the study of not one, but several reactions, it is possible to determine the degree of conjugation of $>\text{C}=\text{C}<$ and $\text{C}=\text{O}$ bonds in relation to the structure of the molecule of the α,β -unsaturated carbonyl compound, and this permits the prediction of the direction of reaction with the latter, and makes it possible to find the typical reaction, which can have analytical significance.

Thus, we proposed to subordinate the study of the chemical properties of compounds with conjugated systems of double bonds to the general study of conjugated multiple bonds, including as well those rules which have been deduced from a consideration of physical properties, among them the regularities observed by K. Auwers [4] with regard to the anomalous values of MR in compounds with conjugated systems.

Without pretending to have made a final decision with regard to the questions here raised, in the present work we present experimental material we have obtained in studying the reactions of introduction of the iodoxy radical, bromination, and the Grignard reaction for a series of α,β -unsaturated ketones.

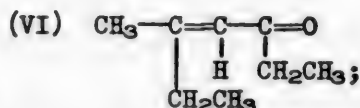
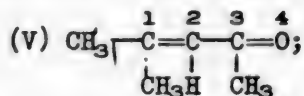
A study of the reaction for introducing the iodoxy radical (Table 1) into α,β -unsaturated ketones shows that ketones with a normal carbon skeleton have the radical introduced with difficulty, even during a lengthy period of reaction. During a 5-minute period of reaction, the transformation of iodine to HI in the mixture does not reach 50%, i.e., iodine unites directly at the $>C=C<$ bond, a fact which once more confirms our interpretation [5] of the course of the reaction for introducing the halo-oxy radical. At the same time, with the increase in mass of the radical of normal structure adjoining carbon 1 of the conjugated system [see butylidene acetone (I) and cenanthyldene acetone (II)] the degree of conjugation of the $>C=C<$ and $>C=O<$ bonds is decreased. This leads to an increase in the value of the iodine number; with (I), it is 1.6%, while with (II) it is 20.9% of theory.

A further comparison of iodine numbers for butylidene acetone (I), butylidene methyl ethyl ketone (III) and butylidene methyl propyl ketone (IV) shows that with an increase of the mass of the saturated, normal radical attached to the CO group:



the iodine number increases,* a fact which must be related to the decrease in the degree of conjugation of the multiple bonds of (I) and (IV).

The introduction of two radicals at carbon 1 of the conjugated system leads to a greater degree of completion of the reaction when a longer period is used to carry it out. The combined influence of methyl and ethyl is greater than that of two methyl groups, a fact which is obvious from the comparison of the magnitudes of the iodine numbers for mesityl oxide (V) and 3-methyl-heptene-3-one-5 (VI):



the iodine number of (V) is 1.8%, that of (VI) 17.6% of theory.

Thus, the greater the mass of the completely hydrogenated radicals attached to carbon 1, the greater the influence in lowering the degree of conjugation.

On the other hand, the introduction upon carbon 1 of radicals with unhydrogenated α -carbons, even of great mass, has a very small influence; the iodine number of 2,2,5,6,6-pentamethylheptene-4-one-3 is 3.8% of theory.

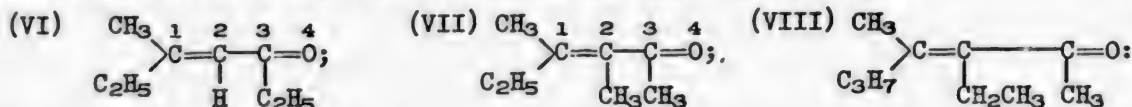
* From (III) to (IV) it is greater than from (I) to (IV); this is explained by the presence in (IV) of a small admixture of 3-ethylheptene-3-one-2, which increases the value of the iodine number of (IV).

Table i

Introduction of the iodoxy group into α,β -unsaturated ketones

Expt. No.	Sample (g)	0.1 N	0.1N	iodine number		0.1 N	Iodine	Duration of reaction, (min)
		Na ₂ S ₂ O ₃ used in titrating excess of halogen(ml)	Na ₂ S ₂ O ₃ equiv. to halogen used up (ml)	found	calc.	Na ₂ S ₂ O ₃ used in titrating I ₂ from HI (ml)	changed to HI (%)	
Butylidene acetone								
1	0.1049	23.51	0.29	3.50	224.46	0.02	6.89	5
2	0.1263	23.41	0.39	3.91		0.02	5.12	5
3	0.0859	25.73	1.88	27.63		1.48	79.14	1370
4	0.0923	25.26	2.34	32.18		2.00	85.47	1370
Butylidene methyl ethyl ketone								
5	0.0759	27.67	0.38	6.35	201.29	0.10	26.31	5
6	0.0768	27.68	0.37	6.11		0.12	32.43	5
7	0.0968	25.64	1.96	25.70		1.32	67.34	1320
8	0.0780	26.33	1.21	19.69		0.95	78.50	1320
Butylidene methyl propyl ketone								
9	0.0892	21.15	1.72	24.47	181.16	0.18	10.46	5
10	0.1118	20.65	2.22	25.20		0.40	18.00	5
Benzylidene acetone								
11	0.0619	29.19	0.25	5.12	173.78	-	-	5
12	0.1028	29.20	0.24	2.96		-	-	5
13	0.0640	28.68	0.76	15.07		0.12	15.8	1350
14	0.0640	28.50	0.94	18.64		0.16	17.0	1350
Benzylidene methyl ethyl ketone								
15	0.1187	36.85	0.82	8.76	158.70	0.30	36.58	5
16	0.1166	37.13	0.54	5.87		0.20	37.03	5
Mesityl oxide								
17	0.0630	29.29	0.16	3.22	258.83	-	-	5
18	0.0388	29.24	0.20	6.54		-	-	5
19	0.0673	23.75	5.59	105.43		2.62	46.86	1740
2,2,5,6,6-pentamethyl heptene-4-one-3								
20	0.0958	32.41	0.36	4.76	139.34	0.13	36.11	5
21	0.1042	32.27	0.50	6.09		0.22	44.00	5
3-methylheptene-3-one-5								
22	0.0700	27.42	2.02	36.62	201.29	1.87	92.57	5
23	0.1204	26.17	3.27	34.47		3.12	95.41	5
24	0.0750	20.18	9.26	156.71		5.48	59.18	1700
25	0.0845	19.22	10.22	153.51		6.54	63.99	1700
3,4-dimethylhexene-3-one-5								
26	0.0498	24.22	3.78	96.34	201.29	2.61	69.04	5
27	0.0579	23.93	4.07	89.22		2.66	65.35	5
28	0.0807	43.26	12.64	198.81		10.12	80.06	1410
29	0.0813	42.87	13.03	204.41		10.27	78.97	1410
3-methyl-4-methylheptene-3-one-2								
30	0.0840	15.84	7.26	109.70	164.68	5.99	82.49	5
31	0.0437	16.96	6.14	105.74		4.44	72.31	5
oenanthyldene acetone								
32	0.1054	35.13	2.54	30.58	164.68	1.02	40.15	5
33	0.1459	33.27	4.40	38.28		1.85	42.04	5

The supplementary introduction of a radical at carbon 2 of the conjugated system leads to a sharp increase of the iodine number. Consequently, its influence upon the degree of conjugation of the $>C=C<$ and $C=O$ bonds is still greater than the influence of the introduction of two radicals at carbon 1. This can be seen from a comparison of the iodine numbers for (VI), 3,4-dimethylhexene-3-one-5 (VII), and 3-ethyl-4-methylheptene-3-one-2 (VIII):



here too, an increase in the mass of the hydrogenated radical causes a decrease in the degree of conjugation; while the iodine number of (VII) amounts on an average to 46%, that of (VIII) has already attained 65% of theory.

On the basis of what has been said, the possibility is suggested of utilizing the reaction for introduction of the iodoxy group to explain, in the first place, the degree of conjugation of the $>C=C<$ and $C=O$ bonds, or in other words, the degree of independence of the ethylene bond in α,β -unsaturated ketones, and in the second place, for a preliminary determination of the structure of the carbon skeleton of the molecule.

A parallel study of the bromination of α,β -unsaturated ketones (Table 2) leads to the following conclusions.

The bromination of α,β -unsaturated ketones with normal structure proceeds in such a manner, that the individual iodine numbers, calculated on the basis of bromine used, up, reach 82 to 97% of theory. At times these numbers correspond to an increased, and at times to a decreased degree of conjugation of the $>C=C<$ and $C=O$ bonds. Here, too we find again the rule on the influence of the mass of the radicals attached to carbon 1 or 3 of the conjugated system; the iodine number of (I) is 86.9%; of (II), 92.6%; of (III), 93%; and of (IV); 87.7% of theory. It is characteristic that the aromatic radical at carbon 1 (see benzylidene acetone, benzylidene methyl ethyl ketone) shows a strong stabilizing effect on the dibromide formed, and the bromination reaction is characterized either by the complete absence of HBr or by the separation of negligible quantities.

The analogy in the behavior of α,β -unsaturated ketones in the iodoxy and bromination reactions can be seen further from the examples of ketones (V) and (VI). Ketone (VI) has weakly conjugated $>C=C<$ and $C=O$ bonds, and during bromination separates much more HBr, so that its iodine number reaches only 58.4% of theory.

What has just been said does not by any means contradict what has been said earlier, that with a decrease of the degree of conjugation of the $>C=C<$ and $C=O$ bonds the iodine numbers increase. The fact is that the capability of ketone (VI) for adding bromine is much greater than that of (V) (see total iodine number) and also than that of ketones of normal structure, but by virtue of the relatively great degree of independence of the ethylene bond and its structure as a trisubstituted ethylene, ketone (VI) easily splits off the elements of HBr in the process of bromination [8].

But the greatest screening effect is shown when a radical is introduced at carbon 2; in 3,4-dimethylhexene-3-one-5, the ethylene bond reacts practically independently. The ketone in question may be regarded as a tetrasubstituted ethylene, giving an unstable dibromide which easily splits off the elements of HBr [8]. The actual iodine number of ketone (VII), calculated by the usual method, is only 13.7% of theory.

*The iodine number of (IV) is actually somewhat lowered; the (IV) is mixed with 3-ethylheptene-3-one-2, and the latter increases the iodine number by substitution.

Table 2

Bromination of α,β -unsaturated ketones in CCl_4 medium.

Expt. No.	Sample (g)	Amount $\text{Br}_2\text{-CCl}_4$ solution (ml)	0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ used in titrating excess iodine (ml)	0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ equiv. to iodine used up (ml)	Total Iodine No.	0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ used to titrate I_2 from HI (ml)	Iodine number of substitution	Iodine number of addition
Butylidene acetone								
1	0.1132	4.5	35.62	19.58	210.71	0.76	17.04	193.67
2	0.1177	6.89	48.65	21.06	228.05	1.48	31.92	195.63
Butylidene methyl ethyl ketone								
3	0.0893	4.05	39.35	14.49	205.95	0.74	21.04	184.91
4	0.0703	4.13	42.66	12.00	216.66	0.75	27.08	189.58
Butylidene methyl propyl ketone								
5	0.0926	8.90	20.69	15.01	205.75	1.77	48.52	157.23
6	0.0965	10.40	25.90	15.82	208.08	1.80	47.35	160.73
Oenanthyldene acetone								
7	0.0581	6.0	35.61	8.22	179.58	0.40	17.47	162.11
8	0.0906	6.0	31.77	12.06	168.96	0.50	14.01	154.95
Benzylidene acetone								
9	0.0969	11.45	32.61	12.27	160.72	—	—	160.72
10	0.0950	15.63	49.22	12.04	160.87	—	—	160.87
Benzylidene methyl ethyl ketone								
11	0.1096	10.08	25.35	12.19	141.17	0.27	6.25	134.92
12	0.1389	10.08	21.69	15.85	144.84	0.48	8.77	136.07
Mesityl oxide								
13	0.1182	9.8	15.55	24.14	259.23	0.50	10.73	248.50
14	0.1482	9.94	9.91	29.94	256.43	0.60	10.28	246.15
2,2,5,6,6-Pentamethyl heptene-4-one-3								
15	0.1382	10.00	24.24	14.88	136.66	1.23	22.59	114.07
16	0.1539	10.00	22.76	16.36	134.93	1.17	19.29	115.64
3-Methylheptene-3-one-5								
17	0.1122	14.75	32.81	26.33	297.86	7.90	178.35	119.01
18	0.1420	16.86	33.92	33.68	301.05	10.48	187.35	113.70
3,4-dimethylhexene-3-one-5								
19	0.0809	17.80	24.46	21.08	330.74	9.93	311.59	19.15
20	0.1170	9.58	4.01	32.58	353.45	15.48	335.87	17.58
3-Ethyl-4-methylheptene-3-one-2								
21	0.0611	8.84	22.60	13.15	273.18	5.37	223.12	50.06
22	0.0624	9.00	22.78	13.62	277.05	5.24	213.17	63.88

In connection with what has been said above, the iodine number of ketone (VIII) should amount to 10 to 14% of theory; actually, it is 39% of theory, which is due to the influence of an admixture with the isomeric 4-methylnonene-4-one-6 (see experimental section). On the whole, the bromination reaction also opens up the possibility of orienting oneself with regard to the structure of the carbon skeleton of the α,β -unsaturated ketones.

Let us proceed to a consideration of the data concerning the Grignard reaction on the basis of the α,β -unsaturated ketones obtained in our laboratory (Table 3).

What is at once striking is the lack of correspondence with the conclusions stated earlier with regard to the behavior of α,β -unsaturated ketones with normal structure. In particular, it was to be expected that (II) would give higher yields of diene hydrocarbons than (I), and (IV) higher than (III). Actually, the experimental data show the opposite results.

The cause of this contradiction is revealed upon comparison of the data for mesityl oxide and 2,2,5,6,6-pentamethylheptene-4-one-3 (IX). The latter ketone, which contains a radical $\left[\begin{array}{c} \text{C} \\ | \\ -\text{C}-\text{C}- \\ | \\ \text{C} \end{array} \right]$ having a much greater volume next to the CO group, in accord with the results of Kohler* should have given a lower yield of tertiary alcohols or of the diene hydrocarbons corresponding to them; the experimental data are directly contradictory.

We are here dealing with the fact that (V), as well as ketones (VI), (VII), and (VIII), which have saturated radicals with hydrogenated α -carbons next to the CO group, have a tendency, as Grignard and Blanschon [7] and others have shown, to enolize under the action of the RMgHal , while ketone (IX) is free from this tendency. Taking into account what has been said above, the lowered yields of normal products in the Grignard reaction with (II) and (IV) can be explained by the more strongly expressed tendency of the given ketones to enolize. The same cause, apparently, also explains why despite the higher degree of conjugation of the $>\text{C}=\text{C}<$ and $\text{C}=\text{O}$ bonds in ketones (V) and (VI) in comparison with (VII), the yields of diene hydrocarbons from (V) and (VI) are slightly higher than from (VII). However, if it is impossible on the basis of the yields of diene hydrocarbons to determine the iso structure of the ketone strictly, on the whole, ketones of the type of mesityl oxide do show a much greater degree of independence of the carbonyl group and therefore give the normal products of the Grignard reaction in better yield.

In the course of the Grignard reaction we must consider primarily the addition of RMgHal to the 1,4-positions, and secondarily the reducing action of RMgHal and the influence of ROMgHal in effecting condensation; all these taken together show convincingly how necessary it is to consider carefully the degree of conjugation of the $>\text{C}=\text{C}<$ and $\text{C}=\text{O}$ bonds in α,β -unsaturated ketones, when we base our reasoning on the results of the Grignard reaction.

The material that has been considered above in characterizing the relation between the structure and the degree of conjugation of the $>\text{C}=\text{C}<$ and $\text{C}=\text{O}$ bonds in molecules of α,β -unsaturated ketones, permits us to foresee that ketones of the methylene acetone type must have a limited degree of conjugation, and that starting with this ketone, as the simplest representative, we may arrive at a solution of the problem as a whole. In deciding what to investigate, we must choose only those reactions which will permit us to make comparisons and which may lead to broad generalizations. As one of these reactions, we must consider the hydrolytic cleavage of α,β -unsaturated ketones, which takes place under the influence of alkaline agents; we may expect that ketones of the type $\text{CH}_2=\text{CHCOR}$

* Loc. cit.

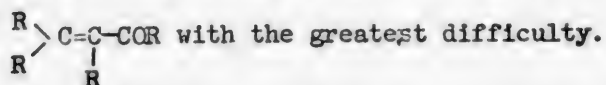
Table 3

Results of the Grignard reaction with α,β -unsaturated ketones

Expt. No.	Structure of hydrocarbon skeletons of original α,β -unsaturated ketones	Grignard reagent	Yield of diene hydrocarbon (% theor.)	
1	Butylidene acetone $C-C-C-C=C-CO-C$	{ CH_3MgI C_2H_5MgBr	41.7 *	[13]
2	$C-C-C-C=C-CO-C$		12.6	[14]
3	Butylidene methyl ethyl ketone $C-C-C-C=C-CO-C-C$	C_2H_5MgBr	38.6	[13]
4	Butylidene methyl propyl ketone $C-C-C-C=C-CO-C-C-C$	C_2H_5MgBr	22.5	[14]
5	Oenanthyldene acetone $C-C-C-C-C-C-C=C-CO-C$	{ CH_3MgI C_2H_5MgBr $iso-C_5H_{11}MgBr$	16.0	[12]
6			12.0	[12]
7			6.2	[12]
8	Isoamylidene acetone $C-C-C-C=C-CO-C$	{ CH_3MgI C_2H_5MgBr	9.5	[14]
9	C		21.5	[14]
10	Mesityl oxide $C-C=C-CO-C$	{ CH_3MgI C_2H_5MgBr $iso-C_5H_{11}MgBr$	38.4	[14]
11	C		50.9	[9]
12			32.9	[10]
13	2,2,5,6,6-Pentamethylheptene-4-one-3 $C-C-C=C-CO-C-C$ $C \quad C \quad C$	CH_3MgI	46.2	[14]
14	3-Methyl heptene-3-one-5 $C-C-C=C-CO-C-C$	{ CH_3MgI C_2H_5MgBr $iso-C_5H_{11}MgBr$	35.7	[14]
15	C		52.9	[11, 13]
16			11.1	[11]
17	3,4-Dimethylhexene-3-one-5 $C-C-C=C-CO-C$	{ CH_3MgI C_2H_5MgBr	32.9	[14]
18	$C \quad C$		50.6	[14]

*Yield increased from 29.5% to 41.7%.

will undergo such decomposition most easily, and ketones of the type



The investigations undertaken by us in this direction show what clear results this reaction gives, and confirm the conclusions drawn from the present work.

EXPERIMENTAL

1. For this investigation we used α,β -unsaturated ketones with the constants given below in Table 4.

The methods of obtaining oenanthyldene acetone, 3-methylheptene-3-one⁵, and benzylidene acetone have been described previously. Of the remaining ketones the preparation of those meriting individual consideration will be described later. Here we shall note only that benzylidene methyl ethyl ketone, after a single vacuum distillation, was obtained in the form of prismatic crystals with m.p. 40°, soluble in concentrated H₂SO₄, with a lemon yellow color [8].

Table 4
Constants of α,β -Unsaturated Ketones

No.	Name of ketone	B.p or M.p.	d_4^{20}	n_D^{20}	MR _D	MR _D
					Found	Calc.
1	Butylidene acetone.....	163-165° (740 mm)	0.8520	1.4424	34.80	34.07
2	Butylidene methyl ethyl ketone	175-177° (743 mm)	0.8613	1.4479	39.19	38.69
3	Butylidene methyl propyl ketone.....	183-187° (729 mm)	0.8540	1.4450	43.64	43.30
4	Oenanthyldene acetone.....	109-110° (22 mm)	0.8473	1.4480	48.70	47.92
5	Isoamylidene acetone.....	174-178° (748 mm)	0.8470	1.4409	39.28	38.68
6	Mesityl oxide.....	129-130° (746 mm)	0.8602	1.4446	30.40	29.45
7	3-Methylheptene-3-one-5.....	164° (752 mm)	0.8591	1.4421	38.85	38.68
8	3,4-Dimethylhexene-3-one-5....	157-158° (746 mm)	0.8585	1.4418	38.85	38.68
9	3-Ethyl-4-methylheptene-3- -one-2.....	187-191° ** (746 mm)	0.8543	1.4450	48.02	47.92
10	2,2,5,6,6-Pentamethyl- heptene-4-one-3.....	202-203° (745 mm)	0.8525	1.4461	56.99	57.16
11	Benzylidene acetone.....	M.p. 42.5°	-	-	-	-
12	Benzylidene methyl ethyl ketone	M.p. 40°	-	-	-	-

2. The introduction of the iodoxy group into ketones was carried out in the following manner. A sample of ketone in a thin-walled glass ampoule was placed in a flask with 10 ml of alcohol and crushed with a glass rod, which was then washed with 10 ml of alcohol. To the alcoholic solution of the ketone was added 25 ml of alcoholic iodine solution; after this had been stirred, 200 ml

* Wide range of boiling temperature explained by 3-methyl heptene-3-one-2 impurity.

** Wide range of boiling temperature explained by 4-methyl nonene-4-one-6 impurity.

of water was added. The reaction mixture was shaken and allowed to remain undisturbed for 5 minutes (for certain ketones, up to 1700 minutes). At the end of the reaction, the excess of iodine was titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution. The amount of iodine transformed into HI was determined by reaction with a solution [of 10 ml of 2% KIO_3 solution, and secondary titration with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ (Table 1)].

3. The bromination of ketones was carried out in CCl_4 solution (10 ml) and after the addition of a solution of bromine in CCl_4 , was allowed to continue for 30 minutes at 0° .

Here, after the addition of KI solution and titration of the excess bromine, the amount of HBr was determined by means of the reaction with KI and KIO_3 (Table 2).

4. The Grignard reaction was carried out by a method worked out by us. *

SUMMARY

1. The degree of conjugation of the $>\text{C}=\text{C}<$ and $\text{C}=\text{O}$ bonds is one of the chief factors determining the reaction tendencies of α,β -unsaturated ketones, and depends upon the number, the chemical nature, and the position of the radicals attached to the carbon atoms of the conjugated system.

2. It has been shown that with an increase in the mass of normal aliphatic radicals attached to carbon 3 of the conjugated system, that is, the CO group, the degree of conjugation of the $>\text{C}=\text{C}<$ and $\text{C}=\text{O}$ bonds is lowered.

3. It has been shown that with an increase in the mass of normal aliphatic radicals upon carbon 1 of the conjugated system the degree of conjugation of the multiple bonds in α,β -unsaturated ketones is lowered.

4. The introduction of two aliphatic, completely hydrogenated radicals at carbon 1 of the conjugated system lowers to a still greater extent the degree of conjugation of the $>\text{C}=\text{C}<$ and $\text{C}=\text{O}$ bonds, the effect of CH_3 plus C_2H_5 being greater than that of two CH_3 groups or of CH_3 plus $\text{C}(\text{CH}_3)_3$.

5. The introduction of hydrogenated aliphatic radicals at carbon 2 of the conjugated system, with two radicals present at carbon 1, exerts a maximum effect upon the degree of conjugation of the $>\text{C}=\text{C}<$ and $\text{C}=\text{O}$ bonds, strongly lowering it. Along with an increase in the mass of the radical, the latter's shielding effect increases.

The reaction for introducing the iodoxy group can be utilized to elucidate the type of structure of the α,β -unsaturated ketones according to the criterion of an increase in the value of the iodine numbers with an increase in the length of the side chains attached to the carbon atoms of the conjugated system.

7. The bromination of α,β -unsaturated ketones in CCl_4 may be utilized to elucidate the type of structure, using as a criterion the lowering of the values of the iodine number of addition (genuine iodine number) with an increase in the number of radicals attached to the carbon atom of the conjugated system.

8. The vinyl ketones have the highest degree of conjugation of the $>\text{C}=\text{C}<$ and $\text{C}=\text{O}$ bonds; as the H atoms attached to the carbons of the vinyl group are substituted by radicals, the degree of conjugation falls; the maximum independence of the $>\text{C}=\text{C}<$ and $\text{C}=\text{O}$ bonds is attained when both carbons of the ethylene bond are quaternary.

* See CB translation this issue p. 1055 ff.

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Received September 8, 1947.

* See CB translation this issue, p. 1055 ff.

THE KINETICS OF THE ESTERIFICATION OF ETHYL ALCOHOL IN THE ABSENCE OF ACID

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Among the products of reaction obtained during the catalytic dehydrogenation of primary alcohols, depending upon the conditions of reaction, such as composition of the catalysts, temperature, etc., are aldehydes, esters and ketones corresponding to the original alcohol, and products with a lengthened hydrocarbon chain in comparison with the original alcohol. Below the optimal temperature interval for esterification, there takes place predominantly the formation of aldehydes; above the interval for esterification, the formation of ketones.

Along with the kinetics of the dehydrogenation of alcohols into aldehydes, we had at the same time the object of investigating [1,2] the kinetics of formation of the remaining products, which has remained unclear up to the present time.

The object of this work was to study the kinetics of the reaction leading to the formation of ester. The realization of this objective was aided by the circumstance that the esterification reaction



was fundamental in determining the temperature interval with copper catalysts, promoted by specially selected added substances.

During the study of the kinetics of the dehydrogenation of alcohol, an important question was the determination of the yield of ester as related to the duration of contact and the partial pressures of the original material, the alcohol, and of the products of reaction, the ethyl acetate and acetaldehyde. In order to express the influence of the reaction products quantitatively, it was convenient to represent this influence by means of so-called relative coefficients of adsorption, related to the time of persistence of the original substances and the products of reaction upon the active centers of the catalyst. It was found [2] that the aldehyde and alcohol have identical adsorption coefficients upon pure copper catalysts. As, in order to study the kinetics of esterification, the most convenient catalyst appeared to be copper with 50% of a special promoter, thus guaranteeing the production as chief product of the reaction of almost pure ethyl acetate (acetaldehyde was obtained only as a minor admixture), the mathematical expression of the kinetics of the dehydrogenation of alcohol to acetaldehyde could not be applied to the process of esterification. It was necessary to introduce mathematical formulas to express the kinetics of esterification.

During the esterification of ethyl alcohol to give ethyl acetate, there were two substances in the reaction mixture: the original ethyl alcohol, and the product of reaction, ethyl acetate.

Even with our catalyst, especially active with regard to the esterification reaction, a small quantity of acetaldehyde was formed, as a secondary product. Over other copper catalysts with promoters, differing in

composition from the one used by us, even under conditions of optimal yield of ethyl acetate, large quantities of acetaldehyde were simultaneously obtained. The reactions for forming acetaldehyde from alcohol, and ethyl acetate from the acetaldehyde are apparently consecutive, and the esterification of alcohol is their resultant.

The relative velocities of formation of these substances over different catalysts vary. Among the products of reaction over a catalyst, therefore, within the definite temperature range, aldehyde may preponderate in one case, and ethyl acetate in another.

In those cases where the chief substance formed is ethyl acetate, we may suppose that of the two consecutive reactions, the dehydrogenation of alcohol, and the condensation of acetaldehyde to ethyl acetate, the condensation reaction is more rapid, and that the velocity of the overall esterification of the alcohol is limited by the dehydrogenation reaction. The latter, as has been shown by various investigators, may be considered a reaction of the first order [2,3]. In order to express the velocity of this reaction, we may utilize the formulas which have been derived on the basis of the adsorption theory of catalysis.

Without taking into consideration the correctness of one or another theory of adsorption, we may calculate relative adsorption coefficients using simple mathematical expressions for the adsorption isotherm.

If we assume that the velocity of the reaction is proportional to the portion of the surface occupied by the adsorbed alcohol, we may express the velocity of the esterification of the alcohol by the equation:

$$-\frac{dx}{dt} K\sigma = K \frac{bp}{1 + bp + b'p' + b''p''} \quad (1)$$

where σ is the fraction of the catalyst surface covered by adsorbed molecules of ethyl alcohol, p is the partial pressure of the alcohol, p' the partial pressure of the ethyl acetate, and p'' the partial pressure of the hydrogen in the mixture; b , b' , and b'' are the coefficients of adsorption of the alcohol, ethyl acetate, and hydrogen respectively; dx is the amount of alcohol reacting in duration of contact dt , expressed in corresponding units (of C , concentration, or of V , volume). This equation can be simplified if we eliminate unity from the denominator, as investigation [2] has shown that it is negligible. We may also neglect the last term in the denominator, $b''p''$, as b'' ; the adsorption coefficient of hydrogen, is many times smaller than the adsorption coefficients b and b' of the alcohol and ethyl acetate.

We then have the expression:

$$-\frac{dx}{dt} = K \frac{bp}{bp + b'p'} \quad (2)$$

Equation (2) may be simplified if instead of the adsorption coefficients b and b' for the alcohol and ethyl acetate we utilize the quantity $\beta = \frac{b'}{b}$, the ratio of these adsorption coefficients. Using β , formula (2) takes the following form:

$$-\frac{dx}{dt} = K \frac{p}{p + \beta p'} \quad (3)$$

In the case of a fine layer of catalyst, we can express the speed of the reaction by the formula:

$$\frac{\Delta x}{\Delta t} = \frac{kp}{p_{av.} + \beta p'_{av.}}, \quad (4)$$

identical in form with formula (2) for an elementary (infinitesimal) layer of catalyst; the differentials dx and dt correspond to the finite quantities Δx and Δt , which express the amount of alcohol reacting in the period of contact over the entire layer of catalyst, and the partial pressures p and p' have been replaced by $p_{av.}$ and $p'_{av.}$, the partial pressures of the alcohol and ester in the reaction mixture, calculated as arithmetical averages of the initial and final partial pressures of these substances. The premissibility of applying formula (4) is confirmed by the fact that the integration of formula (3) over the entire layer of catalyst gives an expression, which, after having been broken down into a series of terms, and simplified by the elimination of those members which contain small quantities to a high order, leads to the form of equation (4) for the entire thin layer of catalyst.

The unknown quantities which enter into this expression, the velocity constant K , and the relative adsorption coefficient, β , can be found by experiment, if we choose a system with two such equations with two unknowns, K and β . The two equations required may be obtained by experimentally determining the reaction velocity $\Delta x/\Delta t$. In order to do this, it is most convenient to pass above a catalyst a mixture of alcohol and ethyl acetate containing different ratios of these two components. In order that the composition of the mixture may not be greatly changed in the course of the reaction, a thin layer of catalyst is used.

Because of the presence of ethyl acetate among the products of reaction, it is necessary to clarify its role in the kinetics of the esterification reaction. In order to express mathematically the influence of the ethyl acetate upon the velocity of the esterification of the alcohol, we can also utilize an adsorption formula. In an analogous manner, the velocity of esterification of the alcohol is influenced by the acetaldehyde in a manner expressed by the equation:

$$-\frac{\Delta x}{\Delta t} = K \frac{p_{av.}}{p_{av.} + \beta p'_{av.} + \gamma p''_{av.}}, \quad (5)$$

where the symbols have the same significance as in the preceding equation (4) $\gamma = \frac{b''}{b}$ = the relative coefficient of adsorption of acetaldehyde, and $p''_{av.}$ is the average partial pressure of acetaldehyde in the mixture.

Using formulas (4) and (5), we can determine experimentally the velocity constants of the esterification reaction and the relative coefficients of adsorption β and γ for ethyl acetate and acetaldehyde obtained in the dehydrogenation of alcohol, using the average values of the partial pressure obtained in the experiment. The coefficients β and γ represent the influence of the ethyl acetate and acetaldehyde upon the velocity of the esterification reaction, and in addition, in their physical sense, can give the quantitative value of this influence.

Setup and Results of Experiments, and Consideration of the Data Obtained

Apparatus and order of conducting experiments. The experiments for studying the kinetics of the reaction were conducted in apparatus depicted schematically in Fig. 1. The introduction of the ethyl alcohol or the mixture of alcohol and ethyl acetate or acetaldehyde into the reactor was carried out continuously from a graduated burette; the alcohol was displaced by mercury, which was admitted from a dropping funnel. For convenience in the work, the

* At two different relative partial pressures $p_{av.}$ and $p'_{av.}$ for alcohol and ethyl acetate.

two burettes were joined in the arrangement. One of them was reserved for the addition of alcohol, the other for the addition of different mixtures. The liquid was passed into a vaporizer, from which it then went through a glass coil (a temperature equalizer) and into the reactor. The reaction products were passed through a water condenser into a condensate collector, cooled by a refrigerating mixture. After the collecting vessel, a supplementary trap followed for the liquid products, also cooled. The remaining aldehyde was caught in a third trap containing hydroxylamine solution. The gaseous products were collected in a gas burette. The reactor was a short tube, of 17 mm diameter, with a perforated glass disc sealed in its lower part; the catalyst was poured upon this. The reactor was placed in an oil thermostat, where it was maintained at the required temperature with an accuracy of 0.5°.

The experiments were carried out over activated copper catalyst. The catalyst was prepared from the acetate or nitrate. The copper acetate or nitrate solution and the promoter were mixed, and precipitated with alkali, in approximately equivalent quantities. The precipitate obtained was washed many times with water by decantation or diffusion. After the water was removed by suction, the paste obtained was dried at 110°.

The dry catalyst was powdered and sifted through a sieve with a 1 mm mesh. It was reduced to copper at 205-210° in a current of hydrogen.

To calculate the kinetics, it was more convenient to have the esterification reaction take place at low depth, so that the greater part of the alcohol did not react. The experiments were therefore conducted at low temperature (170°) and on the fine layer of catalyst, 3.5 cm long.

In these experiments, aqueous alcohol was used; d_4^{20} 0.8045; 94.94% by weight. Ethyl acetate, d_4^{20} 0.8984. Pure acetaldehyde was kept in ampoules, and these shattered before the experiments.

The experiments were conducted with pure alcohol, and with mixtures of alcohol plus acetaldehyde or plus ethyl acetate in definite molecular ratios. The mixture was prepared before the experiment, and its specific weight determined. At the beginning of each experiment, the first portions of the gases and the liquid products were discarded; the experiment was carried out after certain definite conditions were attained. During the time of the experiment, the temperature was measured every 5 minutes, along with the quantity of material introduced into the reactor and the amount of hydrogen obtained by dehydration of the alcohol over the catalyst. To take account of the activity of the catalyst, experiments with mixtures were alternated with experiments carried out with pure alcohol. At the end of the experiment, the condensate was poured out of the trap and immediately weighed. Then the analysis of the condensate was carried out.

Analysis of the products of reaction. After the experiments, acetic acid, acetaldehyde, and ethyl acetate were determined in the condensate. The acetic acid was titrated with 0.1 N alkali using phenolphthalein as indicator.

Determination of acetaldehyde. Acetaldehyde was determined in a separate sample by titration with an ammoniacal solution of silver oxide. When a great quantity of aldehyde was present, part of it was oxidized to acetic acid during the period of titration. The curve (Fig. 2) shows to what extent this oxidation took place. The amount of acetic acid formed during the titration itself was subtracted from the total amount of acetic acid.

Determination of ethyl acetate. Ethyl acetate was determined by saponification of a sample of condensate with 0.1 N NaOH in a flask with a reflux condenser

for one hour, and back titration of the excess alkali. Judging from the data in the literature [4] and from our own observations confirming these data, the amount of ethyl acetate determined by saponification with alkali in the presence of a large quantity of acetaldehyde can give high results. To determine the difference between the true ethyl acetate content and the amount found by analysis, we investigated mixtures of alcohol, ethyl acetate, and acetaldehyde, as well as of ethyl acetate and acetaldehyde. In Fig. 3 is shown the curve for the relationship of the amount of error and the amount of acetaldehyde in the mixture. With 12% of acetaldehyde in the mixture, the error is 0.5%; with 30% of aldehyde, the percent of ethyl acetate found by saponification is higher than the true value by 1.0%; with 50% of acetaldehyde, by 3%, based on the ethyl acetate in the total weight of mixture. The action of alkali upon pure acetaldehyde gave figures corresponding to 8% ethyl acetate. A check on the method of determining ethyl acetate in the presence of acetaldehyde by oxidation of the aldehyde with hydrogen peroxide (according to the method of Lindeken, Clayton, and Skoog [5]) showed no advantages, as in this case too, with a high percentage of aldehyde and little ethyl acetate large errors were found. Therefore, in the analysis of the products of the reaction, we used the method of direct saponification, without preliminary oxidation of the acetaldehyde with hydrogen peroxide, and applied a correction to the error due to the presence of aldehyde.

The determination of ethyl alcohol. Ethyl alcohol was determined by the ethyl nitrite method [8]. Ethyl alcohol in aqueous solution was converted into ethyl nitrite with nitrous acid; the ethyl nitrite was extracted with naphtha, and saponified with hydrochloric acid. The nitrous acid obtained by saponification formed an azo dye with sulfanilic acid and α -naphthylamine. This was determined electrophotometrically.

Selection of the catalyst for kinetic experiments. The dehydrogenation of alcohol takes place upon pure reduced copper at temperatures from 220 to 300° with the formation of almost pure aldehyde [8]. The literature [7] describes various promoters which increase the yield of ethyl acetate, but at the same time there is also a high yield of acetaldehyde. It was necessary to seek a promoter which would increase the yield of ethyl acetate and lower the yield of aldehyde. For this purpose, we prepared a series of catalysts with different added substances, which showed the following results, as listed in Table 1.

For our experiments we took a catalyst containing Cu with 50% promoter. As is evident from the data obtained, the first three catalysts gave a large quantity of acetaldehyde along with the ethyl acetate formed, and only the fourth, containing 50% of promoter, after testing gave a yield of about 24% of ethyl acetate and only small quantities of acetaldehyde and acetic acid. The remainder of the condensate was unreacted alcohol, which in several experiments was determined by the ethyl nitrite method, in the others by difference.

The influence of ethyl acetate. The influence of ethyl acetate upon the velocity of the esterification reaction was studied in mixtures of ethyl alcohol and ethyl acetate in various molecular ratios. At 170°, with a relatively small quantity of ethyl alcohol in the mixtures passed across the layer of catalyst, these experiments gave less and less hydrogen; this was due to the fact that the greater part of the active surface of the catalyst was covered not with the alcohol itself, but with the product of the reaction, the ethyl acetate. If the adsorption coefficients of these two substances had been the same, then the graph obtained for the relation between the amount of hydrogen separated and $\frac{P}{P_{av.} + P_{av.}}$ would have been a straight line. In the case of

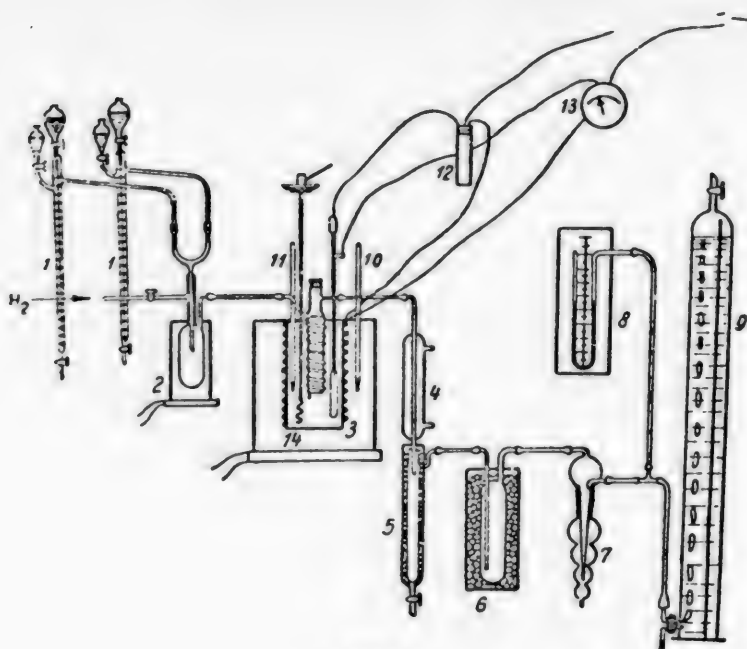


Fig. 1

1-Graduated burettes; 2-heater (vaporizer); 3-reactor; 4-condenser; 5-collector for condensate; 6-supplementary trap; 7-trap with hydroxylamine; 8-manometer; 9-gas burette; 10, 11 thermometers; 12-relay; 13-ammeter; 14-thermostat

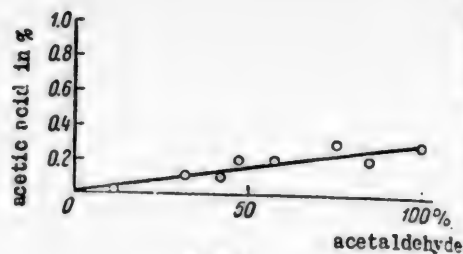


Fig. 2

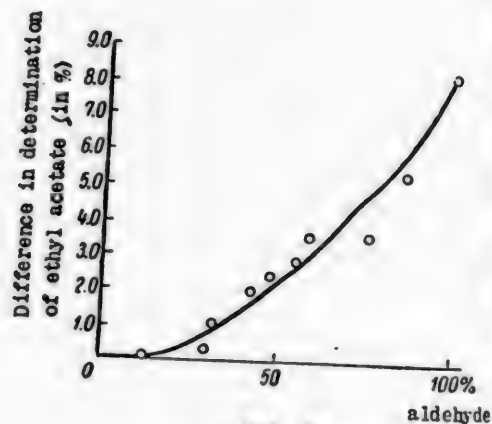


Fig. 3

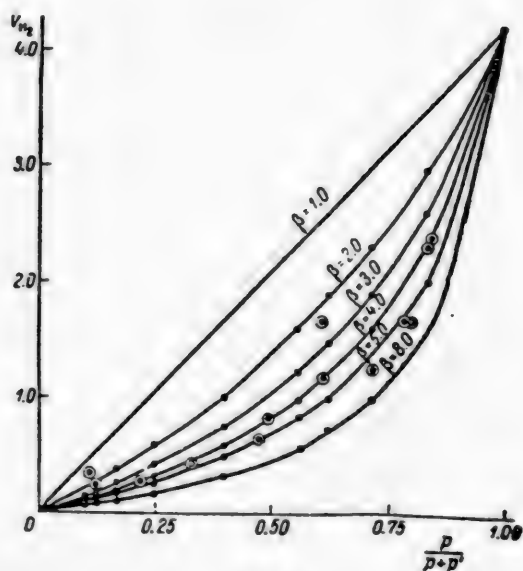


Fig. 4

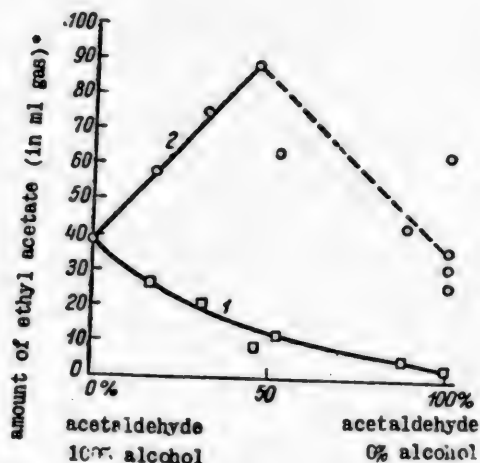


Fig. 5

* calculated for average activity of the catalyst

Table 1

Composition of Catalyst	Thickness of layer of reduced catalyst	Temperature of experiments	Aqueous alcohol 94.94% (g-min)	Composition of condensate obtained			Amount of hydrogen separating in expt. per min.
				Acetic acid %	ethyl acetate %	acetaldehyde %	
Cu + 14% promoter	3.5	200°	0.071	0.2	4.8	6.9	—
	3.5	225°	0.063	1.0	10.9	14.2	—
Cu + 19% promoter	3.5	200	0.074	1.0	9.0	8.2	—
	3.5	225	0.081	2.6	13.3	12.0	—
	3.5	250	0.071	4.6	19.3	15.0	—
Cu + 20% promoter	3.5	200	0.042	1.3	14.7	8.4	—
	3.5	225	0.065	2.1	16.0	13.2	—
Cu + 50% promoter	3.5	180.0	0.055	0.15	14.6	1.9	4.7
	3.5	200.0	0.066	0.30	23.8	3.5	8.8
	3.5	140.0	0.055	0.06	2.4	0.89	0.9
	3.5	140.6	0.047	0.06	2.4	0.87	0.8
	3.5	160.0	0.055	0.04	6.6	—	2.8
	3.5	160.0	0.042	0.58	7.3	1.6	1.8
	3.5	180.0	0.067	0.13	14.0	2.5	5.2
	3.5	200.0	0.057	0.35	23.9	3.9	7.0

Table 2

Experiments with mixtures of alcohol and ethyl acetate

comp. of liq. for expts. (inmole %)		Amounts				time of contact Δt		average partial pressure				vel- ocity const- ant (k)
		substance sup- plied (in%)		hyd. sep. in expt., ml/min.				expts. with mixtures		expts. with pure alcohol		
Aqueous eth- yl alcohol 87.8 mole %	ethyl acetate	pure alcohol	mixture	from pure alcohol	from mixture	for pure alcohol	for mixture	ethyl acetate (p_{av}^i)	alcohol (p_{av}^i)	ethyl acetate (p_{av}^i)	alcohol (p_{av}^i)	
65.0	35.0	0.059	0.067	2.40	0.77	0.154	0.191	0.355	0.551	0.038	0.819	3.0
81.5	18.5	0.069	0.069	3.27	1.37	0.132	0.160	0.194	0.682	0.044	0.812	4.8
75.9	24.1	0.056	0.068	3.57	1.57	0.159	0.159	0.252	0.645	0.0583	0.794	3.0
65.1	34.9	0.058	0.067	3.36	1.57	0.158	0.183	0.355	0.537	0.0537	0.798	3.8
44.2	55.8	0.067	0.071	3.23	0.73	0.133	0.198	0.520	0.340	0.0447	0.809	3.8
36.8	63.2	0.064	0.071	3.79	0.43	0.144	0.214	0.601	0.295	0.0550	0.799	4.9
23.6	76.4	0.061	0.069	3.73	0.30	0.147	0.239	0.742	0.209	0.0558	0.795	4.8
13.6	86.4	0.061	0.072	3.73	0.27	0.144	0.205	0.739	0.097	0.0552	0.799	4.3
13.6	86.4	0.064	0.072	3.73	0.40	0.139	0.205	0.742	0.093	0.0530	0.789	4.0
91.4	8.6	0.064	0.066	3.66	2.46	0.139	0.147	0.104	0.747	0.0530	0.789	6.4
92.0	8.0	0.064	0.066	3.56	2.30	0.142	0.149	0.096	0.759	0.0516	0.802	-
83.0	17.0	0.064	0.067	3.90	1.26	0.147	0.149	0.178	0.708	0.0565	0.795	-
54.3	45.7	0.064	0.070	4.10	0.73	0.141	0.188	0.461	0.410	0.0587	0.793	5.6
0	100	0.064	0.072	4.10	0.17	0.141	-	-	-	0.0587	0.793	-
Average												4.2

different coefficients of adsorption of these substances, part of the products of reaction might be retained on the catalyst and might hinder the further progress of the reaction; this would be expressed in a lower separation of hydrogen, and in place of the straight line, this case would give a curve lying below the line.

In the case we studied, the experimental data obtained, listed in Table 2, were used with equation (4)

$$-\frac{\Delta x}{\Delta t} = \frac{kp_{av.}}{p_{av.} + \beta p'_{av.}},$$

and the velocity constants of the esterification reaction were calculated for the given catalyst. The relative adsorption coefficient, β , was also calculated for every experiment, and a curve drawn showing the relation between the amount of alcohol reacting and the molar composition of the mixture.

For purposes of graphic comparison, (Fig. 4), in the curves sketched on the basis of calculations from equation (4) for different relative coefficients of adsorption, $\beta = 1, 2, 3, 4, 5$ and 8 , the average velocity constant was taken as K ; this value, obtained by experiments with mixtures of alcohol and ethyl acetate was $K = 4.2$. As can be seen from the graph, the points expressing the experimentally found quantities of alcohol reacting were distributed on curves corresponding to a relative adsorption coefficient $\beta = 4$.

The influence of acetaldehyde. The influence of acetaldehyde was studied in mixtures of ethyl alcohol with acetaldehyde in different molecular ratios (Table 3). The calculation of the velocity constant of the reaction was carried out according to equation (5); in this, thanks to preceding experiments, the coefficient β was taken as equal to 4 . The velocity constant calculated by a solution of a system of two equations (5) corresponding to the data, for mixtures of alcohol with aldehyde and for pure alcohol, was equal to 4.15 . The average relative adsorption coefficient of acetaldehyde, calculated from this equation, appeared to be greater than that of ethyl acetate; it was equal to 5 .

Comparison of the roles of alcohol and acetaldehyde in the formation of ethyl acetate during experiments with mixtures of ethyl alcohol and acetaldehyde

In experiments carried out with mixtures of acetaldehyde and ethyl alcohol, it became evident that the amount of hydrogen separated was much less than the amount corresponding to the ethyl acetate formed, as determined by analysis of the condensate from the experiment. In Fig. 5, the relation between the ethyl acetate yield and the molar percentage of components in the mixture is given graphically.

The total amount of ethyl acetate consisted of that obtained in the experiment, plus ethyl acetate obtained as acetic acid, formed as a result of hydrolysis during the experiment. In individual experiments it was found that under the conditions of the experiment, the ethyl acetate underwent hydrolysis. Thus, by the passage over a catalyst of ethyl acetate with water, there were obtained the data given in Table 4, showing that hydrolysis of the ethyl acetate took place.

On the graph (Fig. 5) the ordinate axis represents the value of the ethyl acetate yield, obtained as an average from many experiments conducted with pure alcohol and from parallel experiments with mixtures. The average yield of ethyl acetate in experiments with pure alcohol, expressed in milliliters of gas under standard conditions, as can be seen from the graph, equals 39 . During the gradual addition of acetaldehyde to the alcohol, increased yields of ethyl acetate

Table 3 Experiments with mixtures of ethyl alcohol and acetaldehyde

Composition of liquid for experiments (in mole %)	Amount		Hydrogen separated in experiment (ml/min $\times 10^3$)	Time of contact (hr)	Average partial pressure						Relative Adsorption Coefficient γ	Velocity Constant (K)			
	material added (g/min)				experiments with mixtures			experiments with pure alcohol							
	pure alcohol*	mixture			from pure alcohol		from mixtures								
aqueous ethyl alcohol 87.8 mole %	68.8	31.2	0.064	0.069	3.2	1.4	0.142	0.147	0.230	0.0563	0.632	ethyl alcohol (p_{av})	0.805	4.34	4.19
	48.0	52.0	0.064	0.068	3.1	0.83	0.141	0.151	0.448	0.0543	0.444	ethyl acetate (p'_{av})	0.802	3.14	3.96
	82.8	17.2	0.064	0.067	3.3	1.73	0.141	0.155	0.130	0.0584	0.708		0.791	6.05	4.34
	11.8	88.0	0.064	0.064	3.2	0.33	0.141	0.157	0.845	0.0518	0.099	acetaldehyde (p''_{av})	0.799	-	-
0	100	0.065	0.063	3.2	0.20	-	-	-	-	-	-		-	-	-
0	100	0.065	0.063	3.2	0.27	-	-	-	-	-	-		-	-	-
0	100	0.065	0.063	3.1	0.17	-	-	-	-	-	-		-	-	-
51.5	45.5	0.065*	0.068	3.3	0.60	0.138	0.146	0.390	0.0844	0.487	0.0034	ethyl alcohol (p_{av})	0.784	6.87	4.12
0	100	0.065	0.068	3.5	0.27	-	-	-	-	-	-	average	5.1	-	average 4.15

* For experiment 8 the alcohol used had $d_4^{20} 0.8087$

Table 4 Experiments with Aqueous Ethyl Acetate

Temp. of Expt.	Amount of water in ethyl acetate before expt.	Amount of acetic acid in ethyl acetate before expt. (%)	Amount of acetic acid in ethyl acetate after expt. (%)
170	Ethyl acetate saturated with water about 3%	0.10	1.77
220	Same	0.05	2.86
220	Ethyl acetate with 10% water	0.05	4.16

Table 5 Gradual Poisoning of the Catalyst in Experiments with Acetaldehyde

Temp. °	Catalyst	Composition of Condensate obtained from pure alcohol	acetic acid (%)	ethyl acetate (%)	acetaldehyde (%)
200	Freshly prepared catalyst	0.30	23.8	3.5	
200	Same	0.35	23.8	3.6	
200	Catalyst after 8th expt.	0.23	15.9	1.1	
200	Catalyst after 9th expt.	0.40	12.8	3.8	

were observed, as can be seen from the upper curve, 2, which corresponds to the number of moles of ethyl acetate obtained during experiments (expressed as milliliters of gas and determined in the condensate). Curve 1 on the graph represents the ethyl acetate obtained as a result of the dehydrogenation reaction of the alcohol, calculated on the basis of the amount of hydrogen separated during the reaction.

The lack of correspondence between the hydrogen separated and the amount of ethyl acetate in the condensate testifies to the fact that ethyl acetate is formed from the aldehyde of the mixture itself. This fact also lends probability to the assumption that the formation of ethyl acetate from alcohol also takes place through the intermediate formation of acetaldehyde.

In plotting the graph for the yields of ethyl acetate in relation to the molar percentage of the components of the mixture (Fig. 5), during the gradual increase of acetaldehyde in the mixture there was observed a certain increase of the ethyl acetate yields in comparison with the yields from pure alcohol. In the approach to pure aldehyde, the ethyl acetate yield was lowered, as can be seen from the uppermost point on the curve for pure aldehyde. The final experiments, carried out with pure aldehyde over the same catalyst, gave still greater lowering of the results, which indicated the gradual poisoning of the catalyst. The poisoning of the catalyst was also shown by the fact that after each experiment with acetaldehyde, the catalyst exhibited a lowered activity even in the experiments with pure alcohol, as can be seen from Table 5.

The poisoning was actually greater than appeared to be the case in the experiments with pure alcohol, as the alcohol itself had a tendency partially to decrease the poisoning resulting from the action of the aldehyde.

If the activity of the catalyst had not decreased, the amount of ethyl acetate would have been greater. On the basis of the data obtained, we may conclude that ethyl acetate is formed from alcohol in the same manner as from pure aldehyde.

The assumption that ethyl acetate may be formed by means of condensation of the alcohol itself with acetaldehyde lacks sufficient confirmation.

I. M. Stroyman took part in this work.

SUMMARY

1. It has been found that over copper catalyst containing 50% of promoter, the passage of ethyl alcohol at temperatures from 140 to 200° gives ethyl acetate as chief product of the reaction.

2. It has been shown that the influence of ethyl acetate and acetaldehyde upon the velocity of the ester forming reaction may be expressed by a formula showing the velocity of reaction as dependent upon the partial pressures and adsorption coefficients of ethyl alcohol, ethyl acetate, and acetaldehyde.

3. It has been shown experimentally that ethyl acetate is formed from mixtures of ethyl alcohol and acetaldehyde not only from the alcohol, but from the aldehyde as well; this permits us to consider the acetaldehyde as an intermediate product in the esterification reaction above the catalyst being studied.

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Received October 1, 1947.

THE REACTION OF DIPHENYLMERCURY WITH AROMATIC ALDEHYDES AND KETONES

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The authors have shown previously [1] that diphenylmercury easily enters into reaction with phenols, to form, at 130°, mono- di-, and tri-mercurated derivatives. It became of interest to study the reaction of diphenylmercury with aromatic compounds containing various functional groups.

The reaction of diphenylmercury with benzoic and hydroxybenzoic acids, previously studied by Koton [2], takes place easily at 100 to 120°, with the formation of monomercurated derivatives. The reaction of diphenylmercury with benzaldehyde begins only at 150°, and is accompanied by the separation of metallic mercury (up to 10%) and by considerable tarring, which hinders the isolation of any new derivatives.

The reaction of diphenylmercury with the unsaturated aromatic aldehyde, - cinnamic aldehyde, takes place energetically, with the formation of a great quantity of metallic mercury (up to 46%) and of tar. Only in the case of salicylic aldehyde, which contains along with the aldehyde group a phenolic hydroxyl, does the reaction with diphenylmercury at 150° give the monomercurated derivative, which quickly forms a tar in the air:



Ketones enter into reaction with diphenylmercury with more difficulty. Aromatic ketones (like the aliphatic) do not react with diphenylmercury at 150°. Alkylaromatic ketones (acetophenone) and unsaturated ketones (benzal acetone and benzal acetophenone) do enter into reaction at 150° with diphenylmercury to give the corresponding monomercurated derivatives:



The reaction of diphenylmercury with furfural acetone serves to show that in these reactions the hydrogen atoms in the phenyl groups of the ketones indicated are substituted by the HgC_6H_5 group. In this case, upon the substitution of the benzene ring by the furane ring in the ketone molecule, the formation of mercurated derivatives does not take place; there is observed, instead, the separation of a great quantity of metallic mercury (up to 40%) and considerable tarring. Similarly, the reaction of cyclohexanone with diphenylmercury is observed to give metallic mercury (up to 22%) without the formation of new compounds.

EXPERIMENTAL

All the experiments were carried out by heating the mixture of reacting substances in sealed glass ampoules, placed in an oil thermostat with accurately controlled temperature.

Diphenylmercury and salicylic aldehyde. With 0.5 g of diphenylmercury, 0.3 g of salicylaldehyde was heated at 150° for 3 hours. The reaction mixture was treated with acetone. Upon standing, light yellow crystals separated from the acetone solution. They were recrystallized from petroleum ether. There was obtained 0.15 g with m.p. 81-83°.

0.05 g substance: 2.53 ml 0.1 N NH_4CNS .

0.05 g substance: 2.496 ml 0.1 N NH_4CNS .

Found %: Hg 50.60.

$\text{C}_{13}\text{H}_{10}\text{O}_2\text{Hg}$. Calculated %: Hg 50.35.

The compound obtained was dissolved in acetone and an alcoholic solution of HCl was added; it gave a clear red color, and upon standing, a white crystalline precipitate of phenylmercuric chloride separated out, with m.p. 250-251°, mixed melting point test 250°.

If the reaction is carried out at 150° for 6 hours, strong tar formation takes place, hindering the separation of the monomercurated derivative in pure form.

Diphenylmercury and acetophenone. With 0.3 g of diphenyl mercury, 0.3 g of acetophenone was heated at 150° for 3 hours. The reaction mixture was extracted with cold acetone. The insoluble precipitate was recrystallized from a mixture of alcohol and ether (1:1). There was obtained 0.12 g of crystalline material with m.p. 105-106°.

0.05 g substance: 2.523 ml 0.1 N NH_4CNS .

Found %: Hg 50.46.

$\text{C}_{14}\text{H}_{12}\text{OHg}$. Calculated %: Hg 50.33.

This compound was easily cleaved by an alcoholic solution of HCl with the formation of phenylmercuric chloride, m.p. 250°, in the precipitate. Acetophenone was observed to be present in the solution.

Diphenylmercury and benzal acetone. With 0.7 g of diphenylmercury, 0.2 g benzal acetone was heated at 150° for 3 hours. The reaction mixture was treated with ether; after two recrystallizations from cold ether, 0.3 g of a white crystalline substance was obtained. M.p. 85-87°.

0.05 g substance: 2.36 ml 0.01 N NH_4CNS

Found %: Hg 47.20.

$\text{C}_{16}\text{H}_{14}\text{OHg}$. Calculated %: Hg 47.46.

This monomercurated compound was very easily cleaved by alcoholic HCl with the formation of phenylmercuric chloride, m.p. 249-250°, mixed m.p. 249-250°.

Diphenylmercury and benzal acetophenone. With 0.7 g of diphenylmercury, 0.2 g of benzal acetophenone was heated at 150°, for 3 and 6 hours. The reaction mixture was extracted several times with cold ether, and the product obtained twice recrystallized from cold ether. There was obtained 0.5 g of crystalline material with m.p. 88-90°.

0.05 g substance: 2.09 ml 0.1 N NH_4CNS

Found %: Hg 41.80.

$\text{C}_{21}\text{H}_{16}\text{OHg}$. Calculated %: Hg 41.33.

Under the action of an alcoholic solution of HCl, this compound immediately gave a white crystalline precipitate of phenylmercuric chloride, with m.p. of 250°.

Upon heating of the diphenylmercury at 150° for from 3 to 9 hours with benzophenone, anisole, and fluorenone, no reaction took place. Upon heating of

diphenylmercury at 150° for from 3 to 6 hours with benzaldehyde, cinnamic aldehyde, and furfural acetone, there was observed, in addition to the separation of

The separation of metallic mercury from diphenylmercury during the reaction with aromatic aldehydes and ketones at 150°.

Name of substance	weight (g)	weight of (C ₆ H ₅) ₂ Hg (g)	Duration (hours)	Amount of metallic Hg separated (%)	Note
Benzene.....	0.3	0.3	6	0	No reaction
Styrene.....	0.3	0.3	6	5.3	
Benzaldehyde.....	0.3	0.5	3	4.66	
Benzaldehyde.....	0.3	0.5	6	13.30	
Cinnamic aldehyde.....	0.3	0.5	3	30.75	
Cinnamic aldehyde.....	0.3	0.5	6	46.13	
Phenol.....	0.3	0.3	3	18.35	
Phenol.....	0.3	0.3	6	36.35	
Salicylic aldehyde....	0.3	0.5	3	6.20	
Salicylic aldehyde....	0.3	0.5	6	12.70	
Acetone.....	0.3	0.3	6	0	No reaction
Acetophenone.....	0.3	0.3	6	1.06	
Benzophenone.....	0.3	0.3	6	0	No reaction
Benzalacetone.....	0.3	0.3	3	1.7	
Benzalacetone.....	0.2	0.7	6	6.7	
Benzalacetophenone....	0.2	0.7	6	0	
Furfural acetone.....	0.3	0.3	3	11.94	
Furfural acetone.....	0.3	0.3	6	39.56	
Cyclohexanone.....	0.3	0.3	3	4.53	
Cyclohexanone.....	0.3	0.3	6	22.54	
Fluorenone.....	0.3	0.3	6	0	No reaction
Anisole.....	0.3	0.3	6	0	No reaction

metallic mercury, considerable tar formation. It was impossible to separate any products of the reaction of diphenylmercury with the compounds enumerated above. From the data of the table, the influence of the CH=CH group upon the tendency of aromatic compounds to react is clearly evident. Whereas C₆H₅CHO separates 13.3% Hg from (C₆H₅)₂Hg at 150° in 6 hours, C₆H₅CH=CHCHO gives 46.13% Hg.

Whereas C₆H₆ does not separate Hg at all from (C₆H₅)₂Hg, C₆H₅CH=CH₂ gives 5.3% Hg.

SUMMARY

The reaction of diphenylmercury with salicylic aldehyde, acetophenone, benzal acetone and benzal acetophenone at 150° takes place with the formation of mono molecular derivatives, previously not described in the literature.

The reaction of diphenylmercury with benzaldehyde, cinnamic aldehyde, and furfural acetone at 150° takes place with the separation of metallic mercury (up to 40%) and the formation of tar.

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Received November 9, 1947.

THE REACTION OF AROMATIC MERCURY COMPOUNDS

WITH DIMETHYLANILINE HYDROCHLORIDE

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It has been shown previously [1] that trimethylamine hydrochloride, at 100-130°, easily enters into reaction with diphenyl- and dinaphthylmercury, to form benzene or naphthalene, RHgCl , HgCl_2 , metallic mercury, and free trimethylamine, depending on the conditions of the reaction. It seemed of interest to study the reaction of diphenyl and dinaphthylmercury with the hydrochlorides of aromatic amines. For this purpose, dimethylaniline hydrochloride was prepared, and its reaction with diphenyl- and dinaphthylmercury investigated.

The literature gives no description of this type of reaction. It has been shown that the reaction of diphenyl- and dinaphthylmercury with dimethylaniline hydrochloride is similar in its mechanism, with a few points of difference, to the reaction with trimethylamine hydrochloride.

At 130°, diphenylmercury reacts with dimethylaniline hydrochloride to form benzene, HgCl_2 , and Hg_2Cl_2 ; at 150°, the separation of metallic mercury is also observed. Dinaphthylmercury enters into the reaction with dimethylaniline hydrochloride with more difficulty, at 130° forming naphthalene, HgCl_2 , and Hg_2Cl_2 , and at 150° a small quantity of metallic mercury.

The behavior of the dimethylaniline in this reaction was of considerable interest. In all the experiments, the formation of a violet dye was observed. The formation of this dye, consisting chiefly of pentamethyl parafuchsine, may be explained by the partial isomerization of the dimethylaniline hydrochloride and subsequent hydrolysis and oxidation.

EXPERIMENTAL

Diphenylmercury was obtained by the method of Pfeiffer and Truskeir [2], with m.p. 120-122°. Dinaphthylmercury was obtained by the method of Whitmore and Sobatsky [3], with m.p. 241-243°. Dimethylaniline hydrochloride was prepared by Menshutkin's method [4], in the form of hygroscopic crystals melting at 85-95°. The experiments were conducted at 130 and 150° by heating mixtures of the substance in sealed glass ampoules. After the heating, the ampoules were broken open, and the liquid layer poured off from the solid residue, which was subsequently treated with alcohol, acetone, and ether. After the treatment with solvents, the residue consisted of Hg_2Cl_2 , sometimes mixed with metallic mercury. The mercurous chloride was purified by sublimation and determined iodometrically. The metallic mercury was dissolved in nitric acid and determined by the usual method. The alcohol and acetone solutions were always colored violet and contained Hg^{++} (HgCl_2), whose amount was determined by precipitation as HgS .

To show that the coloring matter formed belonged to dyes of the 'methyl violet' type, we used a qualitative reaction: upon acidification of the solution, the dye color changed, passing through blue and green to orange; in an alkaline medium, it became colorless [5].

Benzene was separated by distillation from the liquid layer, and had

b.p. 80-81°: Naphthalene was separated in pure form, and after recrystallization from a mixture of alcohol and ether had m.p. 79-80°; a mixed test gave m.p. 80°.

All the experiments on the study of the reaction of diphenyl- and dinaphthyl mercury with dimethylaniline hydrochloride are listed in the table.

Temp- era- ture °	Time in hrs.	Name	Weight in g	$C_8H_{11}N \cdot HCl$ in g	Amount, in			Content in %		
					HgS	Hg ₂ Cl ₂	Hg	Hg ⁺⁺	Hg ⁺	Metallic Hg
130	3	Diphenyl- mercury	0.5	0.5	0.16	0.16	—	48.6	48.0	—
130	3	same	0.6	0.6	0.20	0.19	—	50.5	47.5	—
130	6	same	0.5	0.5	0.09	0.25	0.003	27.3	69.1	1.01
150	3	same	0.8	0.8	0.17	0.35	0.012	32.3	65.8	2.6
150	6	same	0.8	0.8	0.15	0.16	0.190	28.5	30.1	42.0
130	3	Dinaphthyl- mercury	0.3	0.3	0.11	0.04	—	72.4	25.7	—
150	3	same	0.3	0.3	0.10	0.015	0.0224	65.1	9.7	17.0
130	3	Mercurous chloride	0.3	0.3	0.065	—	0.1949	22.2	—	77.0
150	3	same	0.3	0.3	0.060	—	0.2037	20.47	—	80.52
150	3	Mercuric chloride	0.3	0.3	—	—	—	100%	—	—

In separate experiments on the heating of HgCl₂ and dimethylaniline hydrochloride, the formation of violet dye took place without the formation of mercurous chloride and metallic chloride. Crystals of the compound $(C_8H_{11}N)_2 \cdot HgCl_2$ were separated, with m.p. 141-143°. In experiments on the heating of mercurous chloride and dimethylaniline hydrochloride, the separation of metallic mercury 77-80% took place; mercuric chloride (20-22%) was formed, and a small quantity of the violet dye.

On the basis of the experiments performed, we may assume that in the reactions with diphenyl- and dinaphthylmercury, the dimethylaniline hydrochloride first decomposes into dimethylaniline and HCl, and the HCl then cleaves the R₂Hg to form RH (benzene or naphthalene) and HgCl₂.

During the reaction of mercuric chloride with dimethylaniline, and the latter's hydrochloride, the violet dye is formed as a result of the reduction of Hg⁺² to Hg⁺¹ and Hg.

SUMMARY

During the reaction of diphenyl- and dinaphthylmercury with dimethylaniline hydrochloride (130-150°) the formation of hydrocarbons (benzene and naphthalene) takes place, as well as of HgCl₂, Hg₂Cl, and a violet dye.

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Received November 9, 1947.

THE CRYSTAL STRUCTURE OF 4-METHYL-5-PHENYL, 1',2', DITHIOL-3-THIONE

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Crystals of 4-methyl-5-phenyl-1,2-dithiol-3-thione, investigated in the present work, were kindly put at our disposal by A.S. Braun, in whose laboratory this compound was first synthesized by M.G.Voronkov.

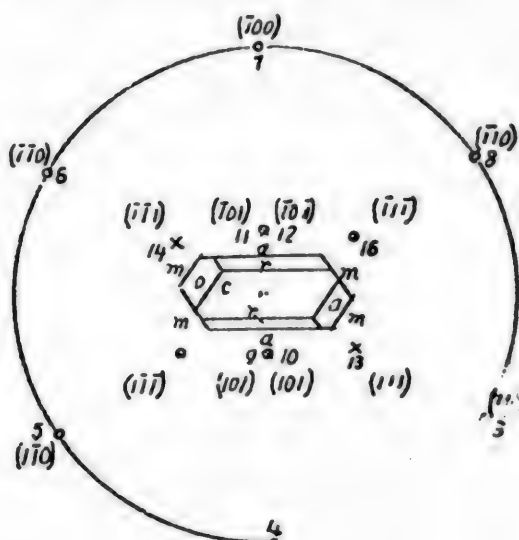
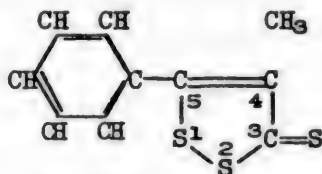


Fig. 1

The empirical formula of the compound is $C_{10}H_8S_3$; its structural formula, determined from the method of synthesis:



The substance consisted of orange-red transparent crystals, of sp. gr. 1.450 g/ml., in the form of long tablets with well-formed faces. For the purpose of goniometric and roentgenographic investigation, the compound was recrystallized from acetone. Its composition corresponded accurately to the formula given above.

1. Determination of Crystal Class

Goniometric measurements were carried out on a two-cycle Fedorov-Flint goniometer, with a precision up to $\pm 2'$. For the purpose of measurement, crystals with dimensions approximately $1 \times 2 \times 5$ mm were chosen. The first determination was along the face [001] the second along [100].

The results obtained are given in Table 1. As is evident from the goniometric measurements and the stereographic projection (Fig. 1), as well as from the presence of direct extinction and optical biaxiality, the crystals under investigation must be referred to the disphenoid class with rhombic syngony $D_2(V) - 222$.

The crystal habit is given in Fig. 1. The crystals consist of prismatic tablets along (100), elongated along 001, with clearly expressed cleavage along (001). Forms a, c are pinacoid; m and r are rhombic prisms; o is disphenoid (Table 1).

The ratio of the axes are $1.6202:1:0.8510$, close to the figures determined from roentgenographic data (see below).

The determination of the Laue class, accomplished by means of a Lauegram, taken through the a axis (Fig. 2), shows the presence of the class $D_{2h}(V_h)$, including $D_2(V)$, C_{2v} and $D_{2h}(V_h)$. A gnomonic projection of the Lauegram, confirming this conclusion, is given in Fig. 3.

Thus, the combination of data obtained determines definitely that the crystals belong to the class $D_2(V)$.

2. Determination of the elementary cell.

To determine the dimensions of the elementary cell, complete rotation roentgenograms were taken about three mutually perpendicular directions, in accordance with the given goniometric measurements.

Rotation roentgenograms were taken with a camera of the Shibold type, with a cylindrical adapter having a radius of 43 mm. Radiation $K_{\alpha\beta} - Fe$, with a Hadding tube, 35 kV, 10 mA. One of the roentgenograms obtained (rotation about the b axis) is given in Fig. 4.

The adapter used was calibrated with a control Debyeogram on KCl. An accurate value of the radius of the adapter was found equal to 43.02 mm, and this value was utilized in the calculations.

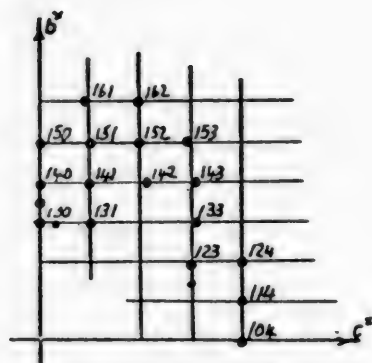


Fig. 3.

Periods of identity were determined along all the cross-sectional lines by rotation roentgenograms. The following values were obtained;

$$a = 14.64 \pm 0.04 \text{ \AA}$$

$$b = 9.05 \pm 0.02 \text{ \AA}$$

$$c = 7.69 \pm 0.02 \text{ \AA}$$

The axis ratios from roentgenographic data $1.6176:1:0.8497$ agree well with the ratios given above, calculated from goniometric measurements. Thus, for example, the exit angle of the normal for the face (110), as determined roentgenographically, is $31^\circ 44'$; the goniometrical measurement gives $31^\circ 41'$.

FIG. 5

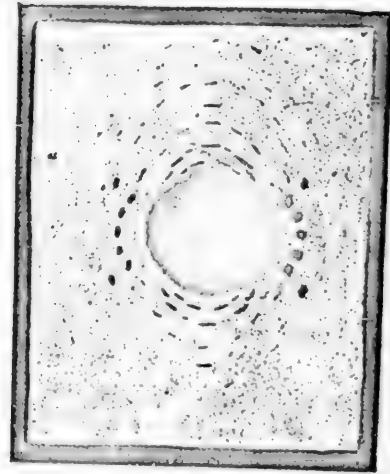
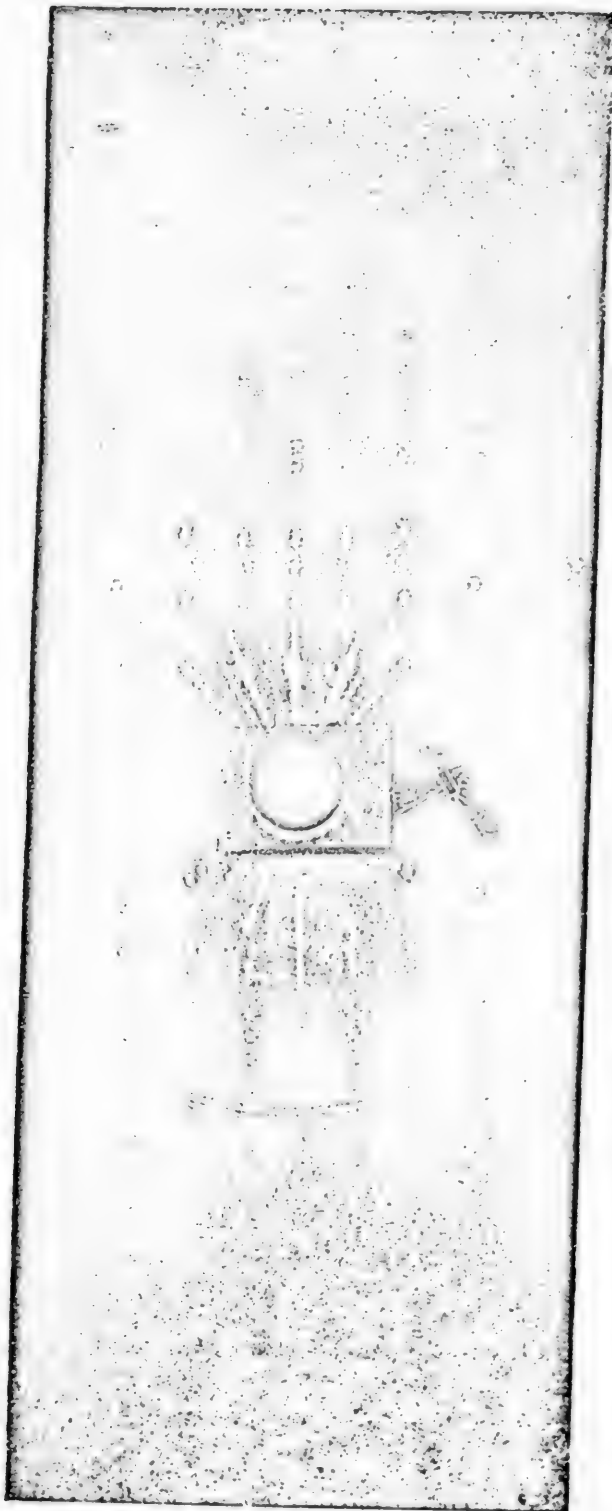


FIG. 2



FIG. 4

The number of molecules in the cell, calculated on the basis of the cell measurements given above and the experimental specific gravity (1.450g/ml) equals 3.97. The roentgenographic specific gravity of the compound is 1.46. Thus, the elementary cell contains 4 molecules.

Table 1
Goniometric measurements of methyl-phenyl-dithiol-thione

Face	Spherical coordinates		Symbols	
	φ	ρ	Of face	Of form
1	0 0	0	001	c
2	0 0	-90°	00 $\bar{1}$	\bar{c}
3	31°41'	90°	110	m
4	90°	90°	100	a
5	148°18'	90°	1 $\bar{1}$ 0	m
6	211°40'	90°	1 $\bar{1}$ 0	m
7	269°55'	90°	100	a
8	328°12'	90°	1 $\bar{1}$ 0	m
9	90°	26°40'	101	r
10	90°	-26°40'	10 $\bar{1}$	r
11	269°55'	26°40'	101	r
12	269°55'	-26°40'	10 $\bar{1}$	r
13	31°41'	45°	111	o
14	211°40'	45°	1 $\bar{1}$ 1	o
15	148°41'	-45°	1 $\bar{1}$ 1	o
16	328°12'	-45°	11 $\bar{1}$	o

3. Determination of the Space Group

The total number of space groups of the class consists of 4 simple and 5 differently centered networks D_2^1 — D_2^5 . To determine the space groups, the necessary data on extinction of reflections were obtained from oscillation roentgenograms. Indications of the latter were produced graphically (with the aid of a reverse network) as proposed by Shibold and worked out in detail by A.I.Kitaygorodsky [1].

Exposure of the oscillation roentgenograms was to copper radiation during oscillation intervals of 13 and 20°, depending on the desired dimensions of the effective region of the reverse network.

Indications of the oscillation roentgenograms, taken along all three axes, showed the absence of reflections of the type hoo, oko, and ool for odd h, k, and l, and the presence of reflections of all the remaining types for all values of h, k, and l (Table 2). The appearance of one of the oscillation roentgenograms is given in Fig. 5.

From a review of the space groups D_2^1 — D_2^5 , the unit group having such extinction is space group D_2^4 , containing 3 spiral axes of the second order and 4 atoms (groups) in general position. Thus, from the data of the roentgenographic investigation, the space group D_2^4 — $P2_12_12_1$ is determined without ambiguity.

Table 2

Observed indices of reflection from oscillation roentgenograms
Radiation - Cu - $K_{\alpha\beta}$; radius of chamber 43.02 mm.

Index of reflection of null line of oscillation roentgenogram						Index of reflection of oscillation roentgenogram along c axis					
along c axis		along a axis		along a axis		1st line	2nd line	3rd line			
J	Index	J	Index	J	Index	J	Index	J	Index	J	Index
mod.	600 β	mod.	040 β	int.	002 β	v.1.	121	v.1.	112	weak	323
v.1.	600	mod.	040	v. int.	002	v.weak	231	v.1.	222	int.	433
weak	800 β	v.1.	051	weak	014 β	int.	331	int.	332	int.	533
int.	800	weak	060 β	int.	014	int.	341	mod	442	mod.	633
weak	910 β	int.	060	weak	015	int.	441	weak	542	weak	743
int.	910	weak	061	int.	025	weak	541	mod.	642	mod.	843
weak	10.10	mod.	062	weak	160 β	int.	551	int.	742	weak	943
mod.	10.20	weak	071	v.weak	026 β	weak	651	mod.	752	weak	10.43
mod.	11.20	weak	072	weak	016	mod.	851	mod.	852	weak	11.43
v. weak	12.30 β	weak	073	mod.	026	v.w.	10.51	weak	952	weak	12.43
weak	12.20	weak	074	weak	046	v.w.	11.51	mod.	10.52	weak	13.43
mod.	12.30	mod.	083	weak	037	mod.	12.51	mod.	11.52	mod.	14.43
v. weak	12.40 β	weak	075	mod.	066	weak	13.51	mod.	12.52	weak	15.53.
weak	14.30 β	weak	084	v.weak	057	weak	16.31	v.w.	14.42		
mod.	12.40	mod.	085	mod.	076	weak	16.41	v.w.	15.32		
int.	12.50	weak	086	mod.	067			mod.	15.42		
weak	13.50	v.weak	077	mod.	086			weak	16.32		
weak	13.60			mod.	077			mod.	17.22		
v.weak	12.70										
int.	14.60										
mod.	13.70										
mod.	12.80										

Note. mod. = moderate.

v.1 = very intense

int. = intense

v.w. = very weak

4. Disposition of the molecules in the elementary cell

Starting from the measurements of the elementary cell of the space group and the assumed form of the molecule, we may try to construct a structure on the basis of the principle of tight packing of the molecules.

The elements of symmetry and the basis of the cell are shown in Fig. 6.

The coordinates of the 4 atoms in general position in group D_2^1 ;

$$1) \quad x, \quad y, \quad z;$$

$$2) \quad \frac{1}{2} + x, \quad \frac{1}{2} - y, \quad \bar{z};$$

$$3) \quad \bar{x}, \quad \frac{1}{2} + y, \quad \frac{1}{2} - z;$$

$$4) \quad \frac{1}{2} - x, \quad y, \quad \frac{1}{2} + z.$$


The role of the atoms must in our case be ascribed to the molecules, schematically shown in the form of an asymmetric triangle.

For the creation of a model of the molecule, two possible variants were considered:

- 1) the benzene and thione rings lying in a single plane;

2) the benzene and thione rings arranged perpendicularly to each other. Both possible forms of the molecule are shown in Fig. 7.

The following interatomic distances were used:

C - H ... 1.09 Å	C - C _{benzene} ... 1.40 Å
C = C ... 1.34 Å	C = S 1.64 Å
S - S ... 2.0 Å	>C - C<..... 1.46 Å
C - S ... 1.74 Å	
C - C ... 1.54 Å	 C - C ... 1.44 Å

The 'half-thickness' of the benzene ring was taken as 1.8 Å, the average of the data of Pauling - 1.85 and Kitaygorodsky - 1.7 Å.

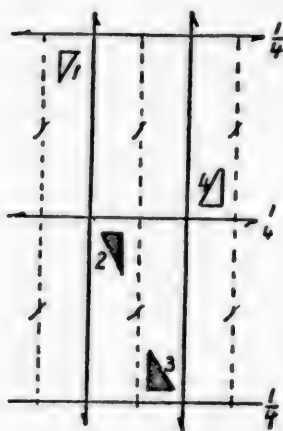


Fig. 6

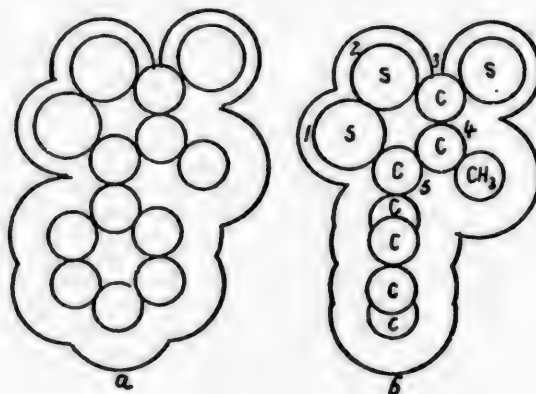


Fig. 7

The intermolecular distance -CH HC- was taken as 3.6 Å.

Under the assumption of a planar form of the molecule, it appeared impossible (in a cell of the given dimensions) to arrange four molecules according to the requirements of the symmetry of the space group $D_2^4(P2_12_12_1)$; it was therefore necessary to assume that the benzene and thione rings were turned with respect to each other.

However, even with this assumption, the packing of the molecules in the form of close-packed ellipsoids, as suggested by Kitaygorodsky [2], was impossible. In this case, the packing had to be carried out in such a manner that the spiral axes had to superpose the protruding parts of one molecule on the hollow parts of another.

Attempts at different variants (using models) led to the following most unique and expedient method of packing.

In the plane of the axes $a = 14.64$ Å and $c = 7.69$ Å, a layer of two molecules was arranged in such a manner that the long axis of the molecule was in this plane at an angle of 38° to the a axis, with the plane of the benzene ring perpendicular to the 'ac' plane (Fig. 8).

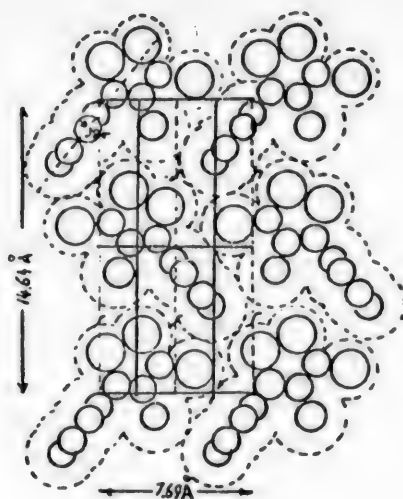


Fig. 8

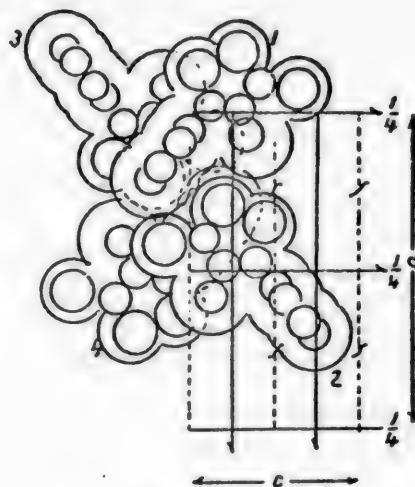


Fig. 9

The area of the molecule in the 'ac' plane: $S_{ac} \cong 54.5 \text{ Å}^2$ (taking account of the intermolecular distances), and using the area of the dinad

$$\eta \cong \frac{2 \cdot 54.5}{14.64 \cdot 7.69} \cong 96.5 \%$$

We may note that the utilization of the area for hexagonal packing of the rings amounts to 91%. Thus, this packing actually makes good use of the area of the dinad, and only in this case permits the possibility of two layers in the direction of the b axis = 9.05 Å.

Actually, with a 'height' of the benzene ring of about 6 Å, the thiol ring of atoms of sulfur with diameter 3 Å will be packed between two benzene nuclei of the upper and lower layers, and the benzene ring of the middle layer between two thiol rings of the upper and lower layers. The experimentally determined distance of 9.05 Å agrees excellently with the sum of the benzene and thiol distances (6 Å + 3 Å).

Thus, the network of the crystal is constructed of a repetition of two identical layers, each of which contains two molecules in a plane of the cell, displaced with respect to each other. The general appearance of the packing in a single (upper) layer is given in Fig. 8. The relative position of the layers is shown in Fig. 9, forming the basis of the cell.

If we characterize the position of the molecule with respect to the axes or the faces of the elementary cell by the position of any atom, for example the C_5 atom in the thiol ring, then its coordinates will be:

$$\begin{aligned} x &= -0.4 \text{ Å} \text{ along the a axis,} \\ y &= 0.0 \text{ Å} \text{ along the b axis,} \\ z &= 0.8 \text{ Å} \text{ along the c axis.} \end{aligned}$$

This kind of packing has much in common with the packing of ellipsoids in the dinad 2_1t of the group $P 2_12_12_1$ [2] with the difference that in our case this packing is accomplished with a completely asymmetrical figure in the plane of the dinad.

• The intermolecular radius of the sulfur was $\sim 1.5 \text{ Å}$.

SUMMARY

The crystal structure of 4-methyl-5-phenyl-1,2-dithiol-3-thione has been studied. The crystals belong to the disphenoid class of rhombic syngony $D_2(V) - 222$. Laue class D_{2h} .

Ratios of the axes 1.6202:1:0.8510: The periods of identity of the elementary cells:

$$a = 14.64 \pm 0.04 \text{ \AA.}$$

$$b = 9.05 \pm 0.02 \text{ \AA.}$$

$$c = 7.69 \pm 0.02 \text{ \AA.}$$

Number of molecules in the cell 4. Space group $P 2_12_12_1 (D_2^4)$.

In the molecule, the planes of the benzene and thiol rings are arranged perpendicularly to each other.

The crystal network is constructed of two layers, each composed of two molecules in the plane of the cell. In the layer of molecules in the "ac" plane, the long axis of the molecule is at an angle of 38° to the a axis. The plane of the thiol ring is in the 'ac' plane, the plane of the benzene ring is perpendicular to it.

In conclusion, we consider it a pleasant duty to express our thanks to A.S.Braun and M.G.Voronkov for supplying specimens of the crystals.

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Received February 10, 1948.

CERTAIN DERIVATIVES OF HYDROXYDIPHENYL

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Hydroxydiphenyl is of interest as a raw material for the manufacture of plastics, antiseptics, bactericides [1], insecticides [2] and for many other uses.

The use of diphenyl is favored by its comparatively low cost, as a mixture of hydroxydiphenyl isomers is obtained as a byproduct in the production of phenol.

Up to the present, a very large number of different hydroxydiphenyl derivatives has been studied, among them the halogen derivatives, nitro compounds, sulfonic acids, and other compounds. Among the least studied derivatives of hydroxydiphenyl are the ethers, and in particular, the ether acids. Of this group of compounds, only 4-phenylphenoxyacetic acid, 2-phenyl-4-bromophenoxyacetic acid and 2-phenyl-4,6-dibromophenoxyacetic acids [3] have been described in the literature.

In this connection, we began our investigation of the synthesis of ether acids and of their simplest derivatives.

We obtained phenylphenoxyacetic acids by the interaction of sodiumphenylphenolates with sodium monochloroacetate or by the saponification of the corresponding amides with caustic soda. The amides and anilides of phenylphenoxyacetic acid were synthesized from the sodium phenolates and chloroacetamide or chloroacetanilide.

It is of interest to note that the velocity of formation of phenylphenoxyacetic acids, both from the phenolates and sodium chloroacetate, as well as by the saponification of the amides, depends greatly upon the structure of the original phenol. Acids form most slowly from dibromohydroxydiphenyl and tribromohydroxydiphenyl. The influence of chlorine is less considerable.

EXPERIMENTAL

1. 4-Phenylphenoxyacetamide and 4-Phenylphenoxyacetanilide

The 4-phenylphenoxyacetamide was synthesized from chloroacetamide and sodium phenylphenolate in isoamyl alcohol, with a yield of 62% of the theoretical. The white crystals melted at 195-196°.

2.389 mg substance: 7.070 mg CO₂; 1.362 mg H₂O.

2.410 mg substance: 7.818 mg CO₂; 1.472 mg H₂O.

Found %: C 74.01, 74.08; H 5.85, 5.72.

C₁₄H₁₃O₂N. Calculated %: C 74.05; H 5.76.

4-Phenylphenoxyacetanilide was obtained by the interaction of chloroacetanilide and sodium phenylphenolate in boiling isoamyl alcohol. Yield, 60%. M.p. 149-150°.

2.389 mg substance: 6.910 mg CO₂; 1.150 mg H₂O.

2.410 mg substance: 6.998 mg CO₂; 1.190 mg H₂O.

Found %: C 79.26, 79.24; H 5.45, 5.53.

C₂₀H₁₇O₂N. Calculated %: C 79.22; H 5.65.

2. 4-Phenyl-2-chlorophenoxyacetic Acid.

4 g of 3-chloro-4-hydroxydiphenyl was dissolved in 50 ml 1.0 N NaOH; 2.8 g of monochloroacetic acid in 12 ml of water was added to the solution, and the mixture was boiled for 5 hours in a flask with a reflux condenser. The 4-phenyl-2-chlorophenoxyacetic acid which separated out was purified by repeated solution in potassium hydroxide and precipitation with HCl, and then by crystallization from dichlorethane. Yield 86%. M.p. 160-161°.

0.1115 g substance: 0.0616 g AgCl.

0.1012 g substance: 0.0561 g AgCl.

Found %: Cl 13.68, 13.73.

$C_{14}H_{11}O_3Cl$. Calculated %: Cl 13.49.

4-Phenyl-2-chlorophenoxyacetamide was obtained by boiling 4.4 g of sodium 4-phenyl-2-chlorophenolate and 1.9 g of chloracetamide for half an hour in 30 ml of absolute ethyl alcohol. Yield 54% (2.8 g). M.p. 164-164.5°.

0.1210 g substance: 0.0652 g AgCl.

0.1305 g substance: 0.0710 g AgCl.

Found %: Cl 13.32, 13.46.

$C_{14}H_{12}O_2NCl$. Calculated %: Cl 13.54.

4-Phenyl-2-chlorophenoxyacetanilide was synthesized in the same manner as the amide. Yield 58%. M.p. 122° (from $C_5H_{11}OH$).

0.1410 g substance: 0.0577 g AgCl.

0.1426 g substance: 0.0603 g AgCl.

Found %: Cl 10.12, 10.20.

$C_{20}H_{16}O_2NCl$. Calculated %: Cl 10.40.

3. 4-Phenyl-2-bromophenoxyacetic Acid

Under the same conditions described for obtaining 4-phenyl-2-chlorophenoxyacetic acid, 4.5 g (75%) of 4-phenyl-2-bromophenoxyacetic acid was obtained from 5 g of 4-phenyl-2-bromophenol, 2.8 g monochloroacetic acid, and 2 g caustic soda.

The 4-phenyl-2-bromophenoxyacetic acid was purified by recrystallization from a mixture of dichlorethane and petroleum ether.

It was a white crystalline substance, m.p. 175.5-177°.

0.1010 g substance: 0.0613 g AgBr.

0.0980 g substance: 0.0603 g AgBr.

Found %: Br 25.84, 26.18.

$C_{14}H_{11}O_3Br$. Calculated %: Br 26.02.

The amide of 4-phenyl-2-bromophenoxyacetic acid was synthesized with a yield of 53% (1.6 g of the amide from 2.5 g phenol). It was purified by crystallization from absolute alcohol. M.p. 167-168.5°.

0.1003 g substance: 0.0620 g AgBr.

0.1102 g substance: 0.0673 g AgBr.

Found %: Br 26.30, 26.00.

$C_{14}H_{12}O_2NBr$. Calculated %: Br 26.11.

4-Phenyl-2-bromophenoxyacetanilide was synthesized in the same manner as the amide. Yield from 5 g of phenol, 3.8 g. M.p. 124°.

0.1215 g substance: 0.0591 g AgBr.

0.1190 g substance: 0.0577 g AgBr.

Found %: Br 20.71, 20.65.

$C_{20}H_{16}O_2NBr$. Calculated %: Br 20.91.

4. 4-Phenyl-2,6-dichlorophenoxyacetic Acid

Under the same conditions described for the synthesis of 4-phenyl-2-chlorophenoxyacetic acid, 4.8 g of 3,5-dichloro-4-hydroxydiphenyl gave 4.3 g (71%) of 4-phenyl-2,6-dichlorophenoxyacetic acid. After three recrystallizations from a mixture of benzene with petroleum ether, the m.p. was 159°.

0.1090 g substance: 0.1039 g AgCl.

0.1072 g substance: 0.1026 g AgCl.

Found %: Cl 23.59, 23.68.

$C_{14}H_{10}O_3Cl_2$. Calculated %: Cl 23.86.

The amide of this acid was obtained in 75% yield (4.5 g amide from 4.8 g of phenol. M.p. 210°, with decomposition.

0.0985 g substance: 0.0960 g AgCl.

0.0930 g substance: 0.0999 g AgCl.

Found %: Cl 24.12, 24.20.

$C_{14}H_{11}O_2NCl_2$. Calculated %: Cl 23.95.

5. 4-Phenyl-2,6-dibromophenoxyacetic Acid

4-Phenyl-2,6-dibromophenoxyacetic acid was synthesized by means of the saponification of the corresponding amide; during its production by the method described above, a large quantity of byproducts was formed, apparently as a result of the partial splitting off of bromine.

2 g of 4-phenyl-2,6-dibromophenoxyacetamide was boiled for 8 hours with an excess of 10% NaOH in a flask with a reflux condenser. After the heating, the reaction mixture was diluted with 300 ml of water and acidified with hydrochloric acid. The acid which separated out was recrystallized twice from petroleum ether. Yield 70%. M.p. 145-146°.

0.0852 g substance: 0.0823 g AgBr.

0.0790 g substance: 0.0726 g AgBr.

Found %: Br 41.12, 41.08.

$C_{14}H_{10}O_3Br_2$. Calculated %: Br 41.40.

4-Phenyl-2,6-dibromophenoxyacetamide was obtained from chloroacetamide and 3,5-dibromo-4-hydroxydiphenyl in isoamyl alcohol. Yield 45%. M.p. 164-165°.

0.0911 g substance: 0.0882 g AgBr.

0.0878 g substance: 0.0852 g AgBr.

Found %: Br 41.22, 41.30.

$C_{14}H_{11}O_2NBr_2$. Calculated %: Br 41.50.

The anilide of 4-phenyl-2,6-dibromophenoxyacetic acid was synthesized in the same way as the amide. From 5 g of 3,5-dibromo-4-hydroxydiphenyl there was obtained 4.7 g of the anilide (70%). White crystals, with m.p. 140-142°.

0.1101 g substance: 0.0886 g AgBr.

0.1028 g substance: 0.0830 g AgBr.

Found %: Br 34.24, 34.37.

$C_{20}H_{15}O_2NBr_2$. Calculated %: Br 34.65.

6. 4-(4'-Bromophenyl)-2-chloro-6-bromophenoxyacetic Acid

4-(4'-Bromophenyl)-2-chloro-6-bromophenoxyacetic acid was obtained in the same way as 4-phenyl-2,6-dibromophenoxyacetic acid. From 3.8 g of amide, 3.5 g of acid (90%) was obtained.

0.1017 g substance: 0.1247 g AgX.

0.0864 g substance: 0.1068 g AgX.

Found %: Cl + Br 46.29, 46.33.

$C_{14}H_9O_3ClBr_2$. Calculated %: Cl + Br 46.44.

4-(4'-bromophenyl)-2-chloro-6-bromophenoxyacetamide was synthesized from chlorodibromohydroxydiphenyl and chloroacetamide in isoamyl alcohol. Yield 60%. M.p. 221-221.5°.

0.0922 g substance: 0.1134 g AgX.

0.0864 g substance: 0.1068 g AgX.

Found %: Cl + Br 46.29, 46.31.

$C_{14}H_{10}O_2NClBr_2$. Calculated %: Cl + Br 46.55.

4-(4'-Bromophenyl)-2-chloro-6-bromophenoxyacetanilide was obtained in the same way as the amide. From 3.6 g of phenol, 1.7 g of anilide was obtained (35%). White crystalline substance. M.p. 205°.

0.0988 g substance: 0.1041 g AgX.

0.0937 g substance: 0.0988 g AgX.

Found %: Cl + Br 39.65, 39.71.

$C_{20}H_{14}O_2NClBr_2$. Calculated %: Cl + Br 39.40.

7. 4-(4'-Bromophenyl)-2,6-dibromophenoxyacetic Acid.

4-(4'-Bromophenyl)-2,6-dibromophenoxyacetic acid was synthesized in the same way as 4-phenyl-2,6-dibromophenoxyacetic acid, by the saponification of the amide. However, in this case, the saponification proceeded much more slowly. Even after 15 hours, complete saponification of the amide had not taken place. From 3.5 g of amide, 1.5 g of acid was obtained (42%).

White crystalline substance. Melting point after two crystallizations from isoamyl alcohol 219.5-220.5°.

0.0995 g substance: 0.1199 g AgBr.

0.0939 g substance: 0.1131 g AgBr.

Found %: Br 51.32, 51.28.

$C_{14}H_9O_3Br_3$. Calculated %: Br 51.56.

The amide of 4-(4'-bromophenyl)-2,6-dibromophenoxyacetic acid was obtained in a yield of 71%, by the interaction of the sodium phenolate with chloroacetamide in isoamyl alcohol (5 g of amide from 6 g of phenol). M.p. 218°.

0.0821 g substance: 0.0991 g AgBr.

0.0911 g substance: 0.1102 g AgBr.

Found %: Br 51.40, 51.51.

$C_{14}H_{10}NO_2Br_3$. Calculated %: Br 51.67.

4-(4'-bromophenyl)-2,6-dibromophenoxyacetanilide was synthesized in the same way as the amide. Yield 50%. M.p. 225.5-226°.

0.1002 g substance: 0.1050 g AgBr.

0.1011 g substance: 0.1062 g AgBr.

Found %: Br 44.61, 44.71.

$C_{20}H_{14}O_2NBr_3$. Calculated %: Br 44.39.

8. 2-Phenylphenoxyacetic Acid

6.8 g of o-hydroxydiphenyl was dissolved in 60 ml of 2.0 N caustic soda, 7.6 g of monochloroacetic acid was added, and the mixture obtained was boiled for 3 hours in a flask with a reflux condenser. At the end of the reaction, a stream of CO_2 was passed through the solution and the precipitate which separated out - the original diphenyl - was filtered off (2.5 g). The filtrate was acidified with hydrochloric acid and the phenylphenoxyacetic acid which separated out was recrystallized 3 times from a mixture of benzene and naphtha. M.p. 109.5-110°. Yield 5 g (87%, calculated on the basis of the hydroxydiphenyl which reacted).

The salts of 2-phenylphenoxyacetic acid and the acid itself are much more

soluble in water than 4-phenylphenoxyacetic acid and its salts.

Although the literature does report the synthesis of 2-phenylphenoxyacetic acid, no data about its properties are given.

0.2073 g, 0.2080 g substance: 18.26, 18.5 ml 0.05 N NaOH.

Found: M 227.0, 225.0.

$C_{14}H_{12}O_2$. Calculated: M 228.2.

2-Phenylphenoxyacetamide was obtained from chloroacetamide and sodium phenylphenolate in absolute alcohol. Yield 70%. M.p. 147°.

4.170 mg substance: 0.243 ml N (26°, 750.7 mm).

7.085 mg substance: 0.410 ml N (26°, 745.7 mm).

Found %: N 6.27, 6.19.

$C_{14}H_{13}O_2N$. Calculated %: N 6.17.

The anilide of 2-phenylphenoxyacetic acid was synthesized in the same way as the amide; however, in this case, isoamyl alcohol was used as a solvent. From 1.7 g of hydroxydiphenyl and 1.7 g of chloroacetanilide, 1.7 g (59%) of the anilide was obtained. The anilide was purified by recrystallization from naphtha. M.p. 112°.

2.530 mg substance: 7.344 mg CO_2 ; 1.310 mg H_2O .

2.802 mg substance: 8.130 mg CO_2 ; 1.425 mg H_2O .

Found %: C 79.22, 79.08; H 5.79, 5.69.

$C_{20}H_{17}O_2N$. Calculated %: C 79.18; H 5.64.

9. 2-Phenyl-4-chlorophenoxyacetic Acid

Under the conditions described for obtaining 2-phenylphenoxyacetic acid, 4.1 g of 5-chloro-2-hydroxydiphenyl and 3.8 g of monochloroacetic acid in 60 ml 1.0 N NaOH gave 2.6 g of 2-phenyl-4-chlorophenoxyacetic acid. After three recrystallizations from petroleum ether, the m.p. was 122°.

0.1844, 0.1860 g substance: 14.0, 14.1 ml 0.05 N NaOH.

Found: M 263.4, 263.8.

$C_{14}H_{11}O_3Cl$. Calculated: M 262.7.

2-Phenyl-4-chlorophenoxyacetamide was obtained in the same manner as 2-phenylphenoxyacetamide (Expt. 8). Yield 49%. M.p. 157-157.5°.

2.429 mg substance: 5.720 mg CO_2 ; 0.980 mg H_2O .

2.622 mg substance: 6.170 mg CO_2 ; 1.091 mg H_2O .

Found %: C 64.26, 64.22; H 4.51, 4.66.

$C_{14}H_{12}O_2NCl$. Calculated %: C 64.25; H 4.65.

2-Phenyl-4-chlorophenoxyacetanilide was synthesized with a yield of 54% of the theoretical. White crystalline substance; after recrystallization from a mixture of naphtha and benzene, m.p. 174°.

10. 2-Phenyl-6-chlorophenoxyacetic Acid

We could not obtain 2-phenyl-6-chlorophenoxyacetic acid in completely pure condition, as upon saponification of the amide in the manner described above, a seriously contaminated product was obtained. The amide and anilide of this acid were obtained in pure form.

2-Phenyl-6-chlorophenoxyacetamide was synthesized with a yield of 41%. From 3 g of 3-chloro-2-hydroxydiphenyl, 0.93 g of chloroacetamide and 0.23 g of sodium hydroxide in 20 ml of isoamyl alcohol, 1.1 g of the amide was obtained.

The white crystalline substance had m.p. 159°.

2.423 mg substance: 5.700 mg CO₂; 1.018 mg H₂O.

2.548 mg substance: 6.010 mg CO₂; 1.110 mg H₂O.

Found %: C 64.20, 64.39; H 4.70, 4.88.

C₁₄H₁₂O₂NCl. Calculated %: C 64.25; H 4.65.

The 2-phenyl-6-chlorophenoxyacetanilide was obtained in 44% yield. The white crystalline substance (from naphtha) had m.p. 112°.

11. 2-Phenyl-4-bromophenoxyacetic Acid.

The 2-phenyl-4-bromophenoxyacetic acid was obtained as described above, in 46% yield. M.p. 137-138°. According to data in the literature, this acid melts at 138°.

The 2-phenyl-4-bromophenoxyacetamide, not described in the literature, was obtained in 50.5% yield. From 5 g of 5-bromo-2-hydroxydiphenyl and the corresponding quantities of the other reagents, 3.1 g of the amide was obtained.

White crystals (from naphtha). M.p. 166°.

8.715 mg substance: 0.375 ml N₂ (29°, 754.4 mm).

8.632 mg substance: 0.365 ml N₂ (27°, 748.5 mm).

Found %: N 4.58, 4.52.

C₁₄H₁₂O₂NBr. Calculated %: N 4.57.

The 2-phenyl-4-bromophenoxyacetanilide was synthesized with a yield of 47%. White crystals; m.p. 164°.

8.785 mg substance: 0.310 ml N₂ (27°, 751 mm).

5.358 mg substance: 0.193 ml N₂ (26°, 751.2 mm).

Found %: N 3.78, 3.88.

C₂₀H₁₆O₂NBr. Calculated %: N 3.67.

12. 2-Phenyl-4,6-dichlorophenoxyacetic Acid

2-Phenyl-4,6-dichlorophenoxyacetic acid was obtained by saponifying the amide. 3 g of 2-phenyl-4,6-dichlorophenoxyacetamide was heated for 3 hours on a water bath with an excess of 10% caustic soda. The salt which separated during the reaction was dissolved in hot water, and the acid precipitated by the addition of dilute HCl.

Yield 2.8 g (92%). After two recrystallizations from naphtha, m.p. 130-130.5°.

0.1865, 0.1830 g substance: 12.4, 12.2 ml 0.05 N NaOH.

Found: M 300.8, 300.0

C₁₄H₁₀O₃Cl₂. Calculated: M 297.1.

2-Phenyl-4,6-dichlorophenoxyacetamide was synthesized with 71% yield. White crystals; m.p. 143°.

2-Phenyl-4,6-dichlorophenoxyacetanilide was obtained from the phenolate and chloroacetanilide in 44% yield. White crystals; m.p. 114.5°.

13. 2-(4'-Chlorophenyl)-4,6-dichlorophenoxyacetic Acid

The 2-(4'-chlorophenyl)-4,6-dichlorophenoxyacetic acid was obtained by saponification of the corresponding amide. From 1.5 g of the amide, 4 hours of heating with 30 ml of 10% aqueous caustic soda gave 1.4 g of the acid. After two recrystallizations from naphtha, the m.p. was 169°.

0.1820, 0.1842 g substance: 11.1 ml, 11.16 ml 0.05 N NaOH

Found M 330.5, 330.1.

C₁₄H₉O₃Cl₃. Calculated M 332.6.

The 2-(4'-chlorophenyl)-4,6-dichlorophenoxyacetamide was synthesized with 48% yield. From 2.7 g of 4',3,5-trichloro-2-hydroxydiphenyl, 0.93 g of chloroacetamide, and 0.23 g of sodium hydroxide in 25 ml of isoamyl alcohol, 1.6 g of the amide was obtained. M.p. 162°.

2-(4'-Chlorophenyl)-4,6-dichlorophenoxyacetanilide was obtained in the same way as the amide. Yield of pure substance 47%. M.p. 113.5°.

14. 2-(4'-Bromophenyl)-4,6-dibromophenoxyacetic Acid

1.5 g 2-(4'-Bromophenyl)-4,6-dibromophenoxyacetamide was heated for 6 hours with 30 ml of a 10% aqueous solution of caustic soda. During the reaction there took place the separation of the only slightly water-soluble sodium salt of 2-(4'-bromophenyl)-4,6-dibromophenoxyacetic acid. The salt was dissolved in 50 ml of hot water, and the free acid was precipitated by the addition of HCl. Yield 1.3 g (85%). The acid obtained was purified by crystallization from a mixture of benzene and naphtha. The melting point of the pure 2-(4'-bromophenyl)-4,6-dibromophenoxyacetic acid was 188°.

0.0685 g, 0.0712 g substance: 2.94, 3.1 ml 0.05 N NaOH.

Found: M 465.9, 459.3.

C₁₄H₉O₃Br₃. Calculated: M 464.9.

2-(4'-Bromophenyl)-4,6-dibromophenoxyacetamide was synthesized with 54% yield. M.p. 198.5°.

The 2-(4'-bromophenyl)-4,6-dibromophenoxyacetanilide was obtained in 39% yield. M.p. 149-149.5°.

SUMMARY

A series of diphenylhydroxyalkylcarboxylic acids not described in the literature, was synthesized and studied, in addition to the simplest derivatives. The majority of the compounds was obtained in completely satisfactory yields.

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Received December 1, 1947.

CYANINE DYES FROM ISOMERIC 2-METHYL-HYDROXYBENZOTHAZOLES

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In 1946, Levkoyev, Sveshnikov, and Heifetz [1] published their work on the synthesis and optical properties of the isomeric dimethoxy thiacyanines. The authors obtained trimethine dyes from all four possible isomers of 2-methyl-methoxybenzothiazole; at the same time, they found that the maximum absorption of the dyes which contained methoxy groups in the 5,5' or 6,6' positions lay further toward the red end of the spectrum than the maximum of dyes with the same substituents in the 4,4' or 7,7' positions. The authors considered this fact as a confirmation of the idea that both heteroatoms, the nitrogen and the sulfur, in the thiazole rings of thiacyanine dyes were similar because of their electronic nature, and that both carried a positive charge.

The work which we have carried out has thrown more light on the question. We set as our objective the synthesis of the four isomeric 2-methyl-hydroxybenzothiazoles, and the formation from these of trimethine dyes of symmetrical and asymmetrical structure, containing hydroxy groups in all possible positions of the benzene ring. It appeared to us that the phenol group, which in alkaline solution was a strong auxochrome, deserved special attention from the point of view of the optical properties of the cyanine dyes. Strangely enough, in contrast to the thiacyanine dyes with methoxy and ethoxy groups, fairly frequently represented in the patent literature [2], the hydroxythiacyanines have up to the present time been completely unknown.

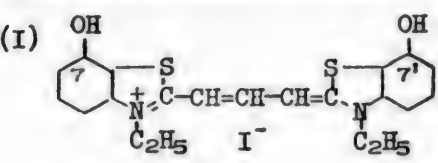
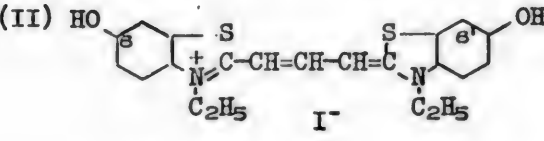
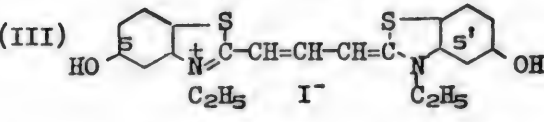
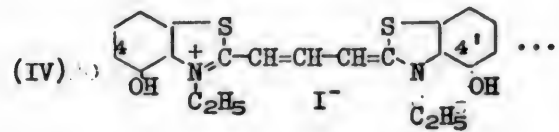
The synthesis of the isomeric 2-methyl-hydroxybenzothiazoles which served as intermediates for the preparation of the dyes which interested us, was carried out by means of acid hydrolysis of the corresponding methoxy derivatives by heating the latter in sealed tubes with concentrated hydrobromic acid. We must note that it is necessary to subject to this kind of hydrolysis the methoxy derivatives of benzothiazole themselves, and not the quaternary salts. The latter, as our experiments have shown, are not only demethylated, but also lose an alkyl group from the nitrogen heteroatom, being converted from the quaternary salts into the hydrobromide salt of the corresponding base.

The hydroxy derivative of 2-methyl benzothiazole thus obtained is converted into the quaternary salt, and the latter condensed by means of orthoformic ester in pyridine to the carbocyanine. The maximum absorptions, measured in alcoholic solution with a Goldberg spectrodensograph, are given in Table 1. They completely resemble those of the corresponding methoxy derivatives, the character of whose absorption curves is closely paralleled by the curves of the hydroxy-cyanines. They can be divided into two groups: 5,5'- and 6,6'-dihydroxythiacyanines are more deeply colored, while the two other dyes, the 4,4'- and 7,7'-dihydroxythiacyanines have a much lighter tint.

The phenol groups in the thiacyanines we obtained are easily acetylated. It is sufficient to grind the dye to powder, then to boil it for a few minutes with acetic anhydride. The intermediate products, the 2-methyl-hydroxybenzthiazoles, can be acetylated and then converted into the acetylated dyes. As a result of acetylation, as was to be expected, we observed displaced maximum absorption in the short wave region of the spectrum. This displacement was much greater

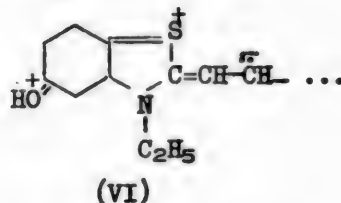
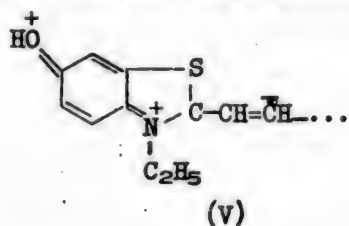
with the 5,5'- and 6,6'- derivatives than with the 4,4'- derivative (we did not obtain the acetylated derivative of the 7,7'-dihydroxy thiocarbo-cyanine); the difference between the maximum absorptions of the isomeric acetoxythiacarbo-cyanines appeared to be very small.

Table 1

Formula of dye	Maximum absorption (in m μ)		
	in neutral solution	in alkaline solution	diacetylated derivative
(I) 	564	569	-
(II) 	576	618	562
(III) 	575	612	567
(IV) 	563	592	562

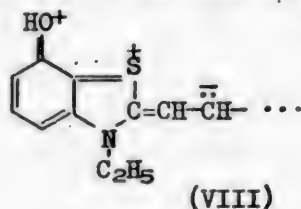
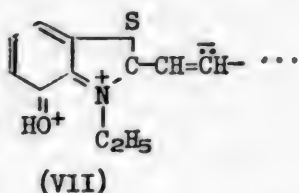
Upon the addition of alkali to the alcoholic solution of the dye, a sharp deepening of the color was observed in the case of the 5,5'- and 6,6'-dihydroxy thiocarbo-cyanines. The violet color of their solutions was changed to pure blue. The character of the absorption curve itself also changed. It became broader, the extinction was lowered, and the maximum was shifted far toward the red end of the spectrum. However, the tints of the 4,4'- and 7,7'-dihydroxy thiocarbo-cyanines showed far less change under the influence of alkali; the change of the 7,7'-dihydroxy derivative was particularly small.

The auxochromic action of the phenol group is related to the displacement of the electron pair of the oxygen atom attached to the benzene ring further along the chain of conjugations:



As the phenol groups in the 5,5'- and 6,6'- positions influence the absorption of light in essentially the same way, there is ground for considering that their

conjugation with the polymethine chromophore takes place across both the nitrogen atom and across the sulfur atom of the thiazole ring [3]. The fact that in the 4- and 7- positions, the action of the phenol group on the color is expressed to a much slighter degree, is, in our opinion, to be explained by the disadvantage of the structure with neighboring charges of the same sign:



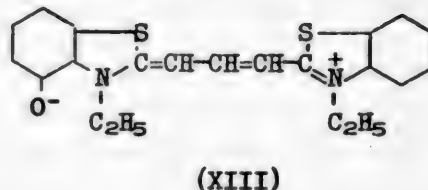
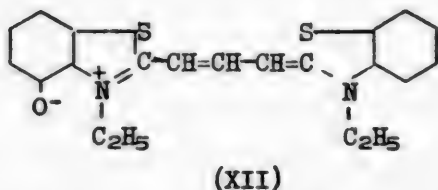
Finally, still other factors must here play a role. Structures (VII) and (VIII) contain strained o-quinoid rings, while structures (V) and (VI) contain the more stable p-quinoid system of bonds. This latter factor, apparently, plays an important role in the alkaline solutions of the dyes.

In addition to the symmetrical dyes, we obtained, using diphenylformamide, the asymmetrical thiacyanines as well, containing the phenol group in only one nucleus. We determined their maximum absorption in neutral and alkaline alcoholic solutions. The results of our measurements are given in Table 2.

In Table 2, special attention is drawn to the fact that between the maximum absorptions of dye (XI) in neutral and alkaline alcoholic solutions, there is hardly any difference. The addition of alkali has hardly any effect upon the color of this asymmetrical dye. The change of color under the action of alkali upon two other dyes, (IX) and (X), is greater, but it is still far from being as great as in the case of the symmetrical preparations.

The surprising behavior of the 4-hydroxy-thiacyanine in alkaline solution forced us to reconsider carefully whether we had actually obtained the dye with a free phenol group, and had not obtained during our preparation the quaternary salt of 4-hydroxy-2-methylbenzothiazole, with an alkylated oxygen atom. The dye was obtained by another method, from 2-methyl-4-acetoxybenzothiazole, and appeared to be identical with the one first synthesized. Analysis threw no doubt upon the purity and the identity of the material.

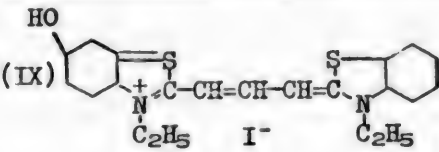
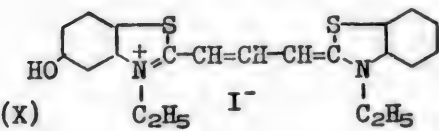
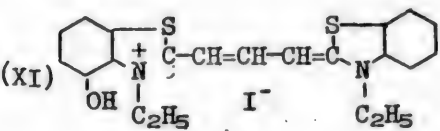
The behavior is without doubt related to the very great lack of equality in the resonance structures of the asymmetrical preparation, as a result of which the 'hypsochrome displacement' (deviation) of the maximum [5] is lowered, reaching a value of 13 mμ. Of the two structures of the dye:



structure (XII) due to the mutual attraction of the neighboring opposite charges, has greater weight in the resonance than structure (XIII). As a result of this, the resonance is weakened, and the color is lightened. With the 5- and 6-hydroxy derivatives, the mutual influence of the charges must appear to a lesser degree.

* The maximum absorption of the symmetrical 4,4'-dihydroxythiacyanine in alkaline solution lies at 592 mμ, the maximum absorption of the unsubstituted thiacyanine at 558 mμ. Calculated as the arithmetical average, the maximum absorption of the asymmetrical 4-hydroxy thiacyanine in alcoholic solution should be at 575 mμ; it was actually observed at 562 mμ. Therefore the hypsochromic displacement equals 13 mμ.

Table 2

Formula of dye	Maximum absorption (in m)		
	in neutral solution	in alkaline solution	acetylated derivative
(IX) 	568	588	-
(X) 	567	577	564
(XI) 	560	562	558

In similar fashion, but still more clearly, we observed the same effect due to the inequality of the structure in the alkaline solution of the asymmetrical thiocarbocyanine containing the phenol group in the 4-position of one nucleus and the nitro group in the 6-position of the other. The hypsochrome displacement of the maximum absorption of this compound (in alkaline solution) equaled 27.5 m μ . Its maximum in neutral alcoholic solution lies at 573 m μ , and in alkaline solution at 561 m μ ; i.e., it is shifted as a result of the addition of alkali by 12 m μ toward the short-wave region of the spectrum. The disturbance of the equivalence of the resonance structure in this case leads to the phenomenon of 'reverse halochromy'. During the formation of the salt, the color of the dye does not deepen, but becomes lighter.

EXPERIMENTAL

Intermediate Products

2-Methyl-7-hydroxybenzothiazole. 1 g of 2-methyl-7-methoxybenzothiazole and 1 g of 48% hydrobromic acid were sealed in a tube and heated at 145-150° for 6 hours. The hydrobromide of 2-methyl-7-hydroxybenzothiazole which separated out in the precipitate was dissolved in a small quantity of weak alkali; the solution was boiled with animal charcoal, and neutralized with acetic acid. 0.75 g of impure base was obtained; after four crystallizations from toluene, 0.3 g, or 33% of theory, was obtained. The compound melted at 192°.

Found %: N 8.37.

C₈H₇ONS. Calculated %: N 8.48.

The quaternary salt of the base was obtained by heating with the ethyl ester of p-toluenesulfonic acid.

2-Methyl-6-hydroxybenzothiazole. 3 g of 2-methyl-6-methoxybenzothiazole was sealed in a tube with 3 g of 48% hydrobromic acid. Heating was continued for 6 hours at 120-130°. Crystals of the hydrobromide of 2-methyl-6-hydroxybenzothiazole which formed during cooling were washed with alcohol and dried. 2.6 g

The m.p. given here and subsequently are uncorrected.

of the salt (63% of theory) was obtained, with m.p. 274-278°.

The hydrobromide was dissolved in a small quantity of alkali, treated while hot with animal charcoal, and the solution accurately neutralized with dilute hydrochloric acid. The 2-methyl-6-hydroxybenzothiazole was recrystallized from toluene. 1.25 g, or 45% of the theoretical was obtained, on the basis of the original methoxy derivative.

The saponification of the 2-methyl-6-methoxybenzothiazole was also carried out with concentrated hydrochloric acid, with heating for 18 hours at 150-160°. The yield of the 2-methyl-6-hydroxybenzothiazole hydrochloride from 1 g of base was 0.8 g, or 72% of theory. The melting point of the hydrochloride was 235-238°. Analysis showed that the salt contained two molecules of water of crystallization.

Found %: N 5.86.

$C_8H_8ONSCl \cdot 2H_2O$. Calculated %: N 5.89.

An experiment was carried out on the saponification with hydrobromic acid of a quaternary salt of 2-methyl-6-methoxybenzthiazole. In this experiment, not only did saponification of the methyl group take place, but the splitting off of alkyl halide as well. 2.6 g of the ethyl iodide of 2-methyl-6-hydroxybenzothiazole was sealed in a tube with 2.6 g of concentrated hydrobromic acid. The heating was continued for 12 hours at a temperature of 130-135°. There was obtained 1.7 g of colorless crystals, with m.p. 274-278°, identical with the crystals of 2-methyl-6-hydroxybenzothiazole hydrobromide previously obtained.

The ethyl iodide of 2-methyl-6-hydroxybenzothiazole was obtained by heating with ethyl iodide in a sealed tube for 12 hours at a temperature of 110-115°. After recrystallization from alcohol, the yield was 79.5% of theory; m.p. 286°.

Found %: I 39.52.

$C_{10}H_{12}ONSI$. Calculated %: I 39.56.

The acetyl derivative of the base was obtained by heating with acetic anhydride for 3 hours on the water bath. Shining needles precipitated from the cold solution. Yield after recrystallization from alcohol, 83%; m.p. 99-100°.

Found %: N 6.72.

$C_{10}H_9O_2NS$. Calculated %: N 6.76.

2-Methyl-5-hydroxybenzothiazole was obtained in exactly the same way as the two preceding bases from the corresponding methoxy derivative. After recrystallization from toluene, the m.p. was 187°; yield 82% of theory.

Found %: N 8.33.

C_8H_7ONS . Calculated %: N 8.48.

The acetyl derivative was obtained after crystallization from alcohol with m.p. 93-94°, yield 87%.

Found %: N 6.90.

$C_{10}H_9O_2NS$. Calculated %: N 6.76.

2-Methyl-4-hydroxybenzothiazole was obtained in the same way as the preceding base. The hydrobromide was obtained in a yield 64% of theory, m.p. 265°. The melting point of the base after recrystallization from toluene was 145°. The compound was easily soluble in water, acids, alkalies, and alcohol, and in benzene and toluene upon heating.

Found %: N 8.37.

C_8H_7ONS . Calculated %: N 8.48.

2 g of 2-methyl-4-hydroxybenzothiazole was dissolved in 6 ml of a 10% aqueous solution of caustic sodium. To the cold solution was added, with shaking, 1.3 ml of acetic anhydride. After crystallization from 50% alcohol, 2 g was obtained, or 80% of the acetyl derivative, with m.p. 79°.

Found %: N 6.76.

$C_{10}H_9O_2NS$. Calculated %: N 6.76.

Dyes

Bis[3-ethyl-7-hydroxybenzothiazole-(2)]-trimethine cyanine iodide (I).

0.8 g of the ethyl-p-toluenesulfonate of 2-methyl-7-hydroxybenzothiazole, 0.8 ml of orthoformic ester, and 4 ml of pyridine were boiled for an hour. The reaction mixture was diluted with water and treated during heating with potassium iodide. The crystals of iodide that precipitated out were recrystallized from alcohol. There was obtained 0.12 g, or 9% of theory; m.p. 251-253° (with decomposition).

Found %: N 5.31.

$C_{21}H_{21}O_2N_2S_2I$. Calculated %: N 5.35.

The same dye was obtained by the saponification of the methoxy group in the trimethine cyanine obtained from 2-methyl-7-methoxybenzothiazole. 0.6 g of bis[3-ethyl-7-methoxybenzothiazole-(2)]-trimethine cyanine iodide and 1.5 ml of 48% hydrobromic acid were heated in a sealed tube for 6 hours at 140-150°. The contents of the tube were diluted with water, and the excess of hydrobromic acid neutralized with ammonia. After the addition of potassium iodide, the compound which precipitated out was recrystallized from alcohol. There was obtained 0.18 g or 34%.

Bis[3-ethyl-6-hydroxybenzothiazole-(2)]-trimethine cyanine iodide (II).

1 g of the ethyl iodide of 2-methyl-6-hydroxybenzothiazole, 1 g of orthoformic ester, and 5 ml of pyridine were boiled for 1 hour. To the resulting solution were added alcohol and water. The dye crystals which separated out were filtered off, washed with water, alcohol, and ether. After crystallization from alcohol, 0.38 g, or 20% of theory, was obtained. M.p. 294° (with decomposition).

Found %: I 21.16.

$C_{21}H_{21}O_2N_2S_2I \cdot 4H_2O$. Calculated % I 21.29.

The dye contained water of crystallization, as was shown by a special test. The same dye was also obtained by the saponification of the trimethine cyanine from 2-methyl-6-methoxybenzothiazole with concentrated hydrobromic acid for 5 hours at 120-130° with 21% yield.

The diacetyl derivative of the dye was obtained in the following manner. 1.5 g of the ethyl-p-toluenesulfonate of 2-methyl-6-acetoxybenzothiazole, 1.5 g of orthoformic ester, and 5 ml of pyridine were boiled together for 1 hour. The solution obtained was evaporated to one third of its volume, and 10 ml of hot alcohol was then added. Upon cooling, the dye crystallized out. It was recrystallized from alcohol; 0.95 g was obtained, or 40% of theory, with m.p. 289-291° (with decomposition).

Found %: N 4.27.

$C_{32}H_{32}O_7N_2S_3$. Calculated %: N 4.36.

Bis[3-ethyl-5-hydroxybenzothiazole-(2)]-trimethine cyanine iodide (III).

This compound was obtained by the saponification of the acetyl group in the corresponding diacetyl derivative. 1 g of the ethyl-p-toluenesulfonate of 2-methyl-5-acetoxybenzothiazole, 1 g of orthoformic ester, and 5 ml of pyridine were boiled for 1 hour. Upon the addition of potassium iodide, the dye was transformed into the iodide. After crystallization from alcohol, 0.35 g, or 24% of theory, was obtained. M.p. 213-215° (with decomposition).

Upon the addition of alkali to the alcoholic solution of this compound, without heating, saponification of the acetyl groups took place in a few seconds, as was evident from the change of color of the solution from violet to blue. The product obtained by saponification did not separate out individually. Analysis of the diacetyl derivative:

Found %: I 20.91.

$C_{25}H_{25}O_4N_2S_2I$. Calculated %: I 20.86.

Bis[3-ethyl-4-hydroxybenzothiazole-(2)]-trimethine cyanine iodide (IV). 1 g of the ethyl-p-toluenesulfonate of 2-methyl-4-hydroxybenzothiazole, 1 g of orthoformic ester, and 5 ml of pyridine were boiled for 1 hour. The pyridine solution of the dye was concentrated by evaporation and treated with a solution of potassium iodide. Coarse violet crystals separated out; these were washed with water, alcohol, and ether. After recrystallization from alcohol, 0.2 g were obtained, or 13% of theory.

Found %: I 22.79.

$C_{21}H_{21}O_2N_2S_2I \cdot 2H_2O$. Calculated %: I 22.84.

The diacetyl derivative of this dye - bis[3-ethyl-4-acetoxybenzothiazole(2)]-trimethine cyanine iodide - was obtained from the ethyl-p-toluenesulfonate of 2-methyl-4-acetoxybenzothiazole, orthoformic ester, and pyridine by heating for 1 hour. After the addition of potassium iodide, the dye was filtered off and recrystallized from alcohol. The crystals were blue; yield 0.2 g, or 13% of theory; m.p. 266-267° (with decomposition).

Found %: I 20.74.

$C_{25}H_{25}O_4N_2S_2I$. Calculated %: I 20.86.

[3-Ethylbenzothiazole-(2)]-[3-ethyl-6-hydroxybenzothiazole-(2)]-trimethine cyanine iodide (IX). 1 g of the ethyl-p-toluenesulfonate of 2-methyl-6-hydroxybenzothiazole, 1.2 g of the ethyl iodide of 2-(ω -acetanilido-vinyl)-benzothiazole ('intermediate product') and 4 ml of pyridine were heated to boiling for 1 hour. After crystallization from alcohol, 0.32 g was obtained, or 21% of theory. For purposes of analysis, the preparation was recrystallized from alcohol three times. M.p. 245° (with decomposition).

Found %: I 24.25.

$C_{21}H_{21}ON_2S_2I \cdot H_2O$. Calculated %: I 24.1.

The presence of water of crystallization in the dye was shown by a special test.

[3-Ethylbenzothiazole-(2)]-[3-ethyl-5-hydroxybenzothiazole-(2)]-trimethine cyanine iodide (X). 1 g of the ethyl-p-toluenesulfonate of 2-methyl-acetoxybenzothiazole, 1.1 g of the 'intermediate product', and 5 ml of pyridine were boiled for 1 hour with a reflux condenser. After recrystallization from alcohol, 0.25 g was obtained, or 17% of theory. M.p. 275°-276° (with decomposition). Upon the addition of alcoholic alkali to the alcohol solution of the dye, the acetyl groups were immediately saponified (change of color). Analysis of the diacetyl derivative:

Found %: I 22.94.

$C_{23}H_{23}O_2N_2S_2I$. Calculated %: I 23.09.

[3-Ethylbenzothiazole-(2)]-[3-ethyl-4-hydroxybenzothiazole-(2)]-trimethine cyanine iodide (XI). 0.5 g of the ethyl-p-toluenesulfonate of 2-methyl-4-hydroxybenzthiazole, 0.55 g of the intermediate product, and 3 ml of pyridine were heated to boiling for 1 hour. After the addition of potassium iodide and recrystallization from alcohol, 0.14 g was obtained, or 20% of theory.

Found %: I 24.77.

$C_{21}H_{21}ON_2S_2I$. Calculated %: I 24.60.

The acetyl derivative of this dye was obtained in the same way from the ethyl-p-toluenesulfonate of 2-methyl-4-acetoxybenzothiazole with a yield of 16% of theory, with m.p. 263-264° (with decomposition).

Found %: I 22.90.

$C_{23}H_{23}O_2N_2S_2I$. Calculated %: I 23.09.

[3-Ethyl-4-hydroxybenzothiazole-(2)]-[3-ethyl-6-nitrobenzothiazole-(2)]-trimethine cyanine iodide. 0.5 g of the ethyl-p-toluenesulfonate of 2-methyl-4-acetoxybenzothiazole, 0.6 g of the ethyl iodide of 2-(4'-acetanilidovinyl)-3-ethyl-4-acetoxybenzothiazole, and 5 ml of pyridine were boiled for 45 minutes. Fine crystals with a metallic luster precipitated out; they were filtered off and washed with alcohol and ether. As the compound was practically insoluble in alcohol, the purification was carried out by boiling in alcohol and washing with hot alcohol. M.p. 278-279° (with decomposition). Yield 24% of theory. Upon the addition of alkali, the dye was quickly converted into the hydroxy-nitro derivative with a change in the color of the solution.

Found %: N 6.78.

$C_{23}H_{22}O_4N_3S_2I$. Calculated %: N 7.06.

SUMMARY

1. Symmetrical thiocarbocyanines have been synthesized with two phenol groups in the 7,7', 6,6', 5,5', and 4,4' positions, asymmetrical thiocarbocyanines with a single phenol group in the 6-, 5-, and 4- positions, and also the acetyl derivatives of these dyes.

2. The four isomeric 2-methyl-hydroxybenzothiazoles, obtained by the demethylation of the corresponding 2-methyl-methoxy-benzothiazoles with hydrobromic acid, served as intermediates in the synthesis.

3. Like the methoxy groups, the phenol groups deepened the color of the thiocarbocyanines much more strongly when in the 6,6'- and 5,5'- positions, than in the 7,7'- and 4,4'- positions. Under the influence of alkali, the band of maximum absorption of the 6,6'- and 5,5'- dihydroxythiocarbocyanines was considerably shifted toward the long-wave portion of the spectrum; the shift of the maximum of the 4,4'-dihydroxy derivative was much less; the 7,7'-dihydroxythiocarbocyanine hardly changed color under the influence of the alkali.

4. Asymmetrical dyes containing one phenol group were of lighter color than the symmetrical. The addition of alkali influenced their color less than the color of the symmetrical dihydroxythiocarbocyanines. The absorption of light by 4-hydroxythiocarbocyanine was hardly changed by the action of alkali. In the case of the dye containing the phenol group in the 4- position in one nucleus and the nitro group in the 6 position in the other, the addition of alkali to the alcoholic solution of the dye displaced the maximum of absorption not toward the long wave, but toward the short-wave part of the spectrum.

5. The authors have suggested an explanation of the observed changes of color of the dye solutions in the presence and absence of alkali from the point of view of the resonance theory of structure.

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THE SYNTHESIS OF 3,5-DICHLORO-4-HYDROXY BENZOIC ACID

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The 3,5-dichloro-4-hydroxy derivative of benzoic acid was obtained in 1876 by Lossner [1], by the action of antimony pentachloride of 4-hydroxybenzoic acid.

Later, 3,5-dichloro-4-hydroxybenzoic acid was obtained by Varnholt [2] by treating the potassium salt of dichlorophenol with carbon dioxide at 140°. Zincke [3] found an easier and more convenient method of obtaining this substance by passing chlorine into a 10% acetic acid solution of 4-hydroxybenzoic acid without heating the reaction mixture. If 1 mole of the 4-hydroxybenzoic acid is dissolved in three moles of 15% caustic potash and an excess of a current of chlorine is passed through this solution, with cooling, then a large quantity of an insoluble white compound, 3,5-dichloro-4-hydroxybenzoic acid, is formed in the reaction; this may be collected and purified from traces of dichlorophenol by the not too lengthy action of steam [4]. The action of chlorine on the aqueous solution of 3-sulfo-4-hydroxybenzoic acid gives 3,5-dichloro-4-hydroxybenzoic acid. R.L.Datta and H.K.Mitter [5] recently devised a method of preparation of this compound from 4-hydroxybenzoic acid by means of 3-sulfo-4-hydroxybenzoic acid. A. Leulier and L. Pinet [6] utilized the chlorinating action of hydrochloric acid and perhydrol (H_2O_2) to obtain 3,5-dichloro-4-hydroxybenzoic acid from 4-hydroxybenzoic acid. The product melted at 265°. The reaction had to be carried out with an excess of perhydrol. At the same time as it gave this product, the method also gave 3-chloro-4-hydroxybenzoic acid, with a melting point of 164°. It is also possible to utilize the ethers of 4-hydroxybenzoic acid. D.S.Tarbell and J.W.Wilson treated the ethyl ether of 4-hydroxybenzoic acid with sulfuryl chloride and obtained a good yield of the ethyl ether of 3,5-dichloro-4-hydroxybenzoic acid [7]. The ether was obtained in the form of a monohydrate. After prolonged drying in vacuum over phosphorus pentoxide, it lost as much weight as corresponded to one molecule of water. The product thus dried melted at 111-112°. From the ether, the authors obtained the free 3,5-dichloro-4-hydroxybenzoic acid, which was recrystallized from a mixture of ethanol and water (2:1). The melting point of this product was 264-266°, with decomposition. The product, upon being recrystallized from acetic acid, melted at 268-269°.

More recently, Hopkins and Chisholm [8] have reported that they obtained 3,5-dichloro-4-hydroxybenzoic acid by the chlorination of 4-hydroxybenzoic acid with aqueous sodium hypochlorite at ordinary temperature. The yield amounted to 50%. Actually, we think that in this case we are dealing with a modification of the older method previously worked out by N. Tarugi [4].

All these methods have only a laboratory significance and can be applied to the study of the chemical properties of p-hydroxybenzoic acid. We undertook broader objectives - to find an industrial method of synthesis of 3,5-dichloro-4-hydroxybenzoic acid so that this compound might find technical application.

It has been found, for example, that the acid forms a violet dye with

dimethyl aniline, whose structure has not been more closely investigated. Other applications are also possible.

EXPERIMENTAL

80 g of p-hydroxybenzoic acid with m.p. 210-214° and 200 g of concentrated acetic acid were placed in a three-necked flask, fitted with a mechanical stirrer. During heating to 60-80° and mixing with the stirrer, a steady stream of gaseous chlorine was led in from a cylinder. The end of the reaction was indicated by the precipitation of a snow-white precipitate of 3,5-dichloro-4-hydroxybenzoic acid and a change in the color of the solution from dark yellow to pale yellow. The absorption of chlorine came to a stop, and as a result a yellow color again appeared in the flask. The precipitate was filtered off, dried at a temperature of 100 to 120° in a dessicator, and weighed. Yield, 89 g. From the mother liquid, after distillation of the acetic acid, an additional 65 g of product was separated. The acetic acid which had been distilled off was used for a second experiment. If the filtrate is not concentrated, it can be used for a new experiment, as a solvent for a fresh portion of p-hydroxybenzoic acid. Thus, it is possible to utilize the mother liquid many times. The melting point of the recrystallized product was 265°.

3.719 mg substance: 5.526 mg CO₂; 0.62 mg H₂O.
4.146 mg substance: 6.134 mg CO₂; 0.667 mg H₂O.
Found %: C 40.52, 40.35; H 1.85, 1.80.
C₇H₃O₃Cl₂. Calculated %: C 40.58; H 1.93.
2.621 mg substance: 3.66 mg AgCl.
3.032 mg substance: 4.20 mg AgCl.
Found %: Cl 34.27, 34.54.
C₇H₄O₃Cl₂. Calculated %: Cl 34.30.

SUMMARY

1. All the present methods of obtaining 3,5-dichloro-4-hydroxybenzoic acid have been critically reviewed and compared.
2. A very simple and convenient method of synthesis of 3,5-dichloro-4-hydroxybenzoic acid has been worked out. This method is also applicable to the industrial production of this substance.

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Received May 12, 1947.

INVESTIGATIONS IN THE FIELD OF HYDROXYFUCHSONE DYES

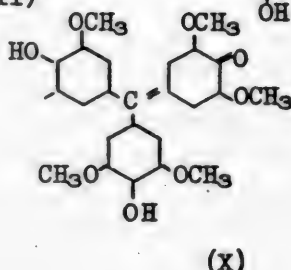
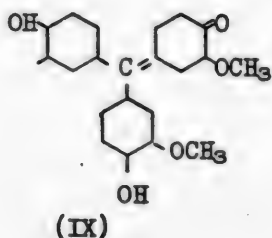
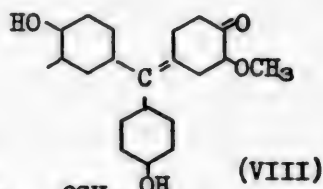
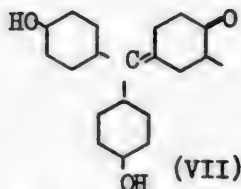
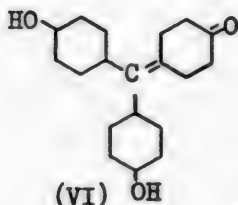
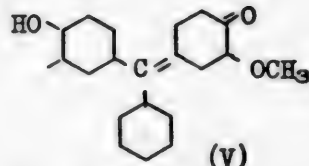
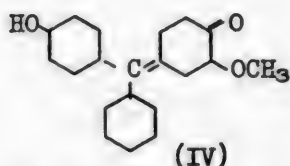
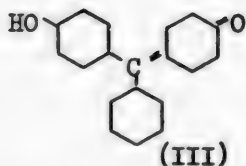
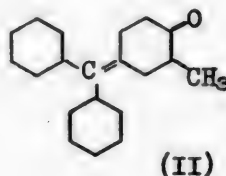
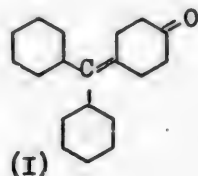
IX. STRUCTURE AND COLOR-PROPERTIES OF HYDROXYMETHOXY FUCHSONES

I. S. Yoffe and A. F. Sukhina

Department of Organic Chemistry of the Military-Naval Medical Academy

In previous communications, we have described a series of new hydroxy-methoxy fuchsones, systematically prepared in our laboratory. We considered it of interest to compare the structure of these dyes with their visual color properties.

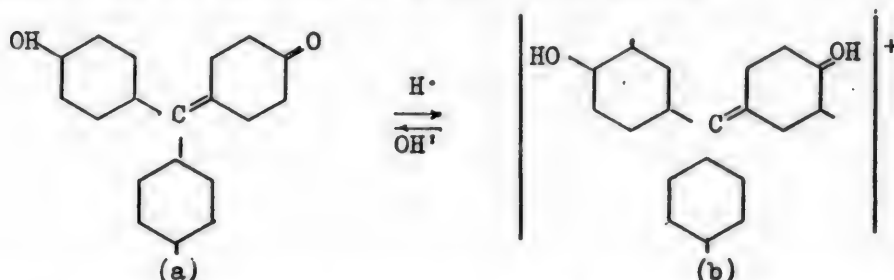
As objects of investigation, we used the following substances: fuchsone (I) [1] and methoxyfuchsone [1](II), benzaurin [2](III), monomethoxy benzaurin [3] (IV), and dimethoxybenzaurin [4] (V), aurin (VI), monomethoxy aurin [5](VII), dimethoxyaurin [5] (VIII), trimethoxyaurin [6](IX), and hexamethoxyaurin [7] (X). All these dyes were purified by passing through the form of bisulfite derivatives, according to the method described by us [8], with subsequent recrystallization from acetic acid or alcohol.



Our investigations were conducted with a Koenig-Martens spectrophotometer in the laboratory of Academician A.E.Porai-Koshits, to whom we express our gratitude for his cooperation in the completion of this research.

In all the determinations, the concentration of dye was chosen so that logarithm 100E at the maximum as a rule equaled 2.

All the substances studied by us had indicator properties [9]. They were soluble in mineral acids with a deepening of color; in this process, apparently, the bearer of the color was the mesomer of the cation (b), formed as a result of the addition of a proton to the quinone oxygen of the hydroxyfuchsone dye. During hydrolysis, this type of cation dissociates with the regeneration of the dye in the hydroxyfuchsone form (a). The equilibrium, using benzaurin as an example, may be expressed by the following scheme:



A preliminary determination of the absorption spectra of several dyes in hydrochloric and sulfuric acid solutions (10% HCl and 20% H₂SO₄) showed such complete agreement that the absorption curves of each of the dyes in both hydrochloric and sulfuric acid solutions absolutely coincide. In this we may see a confirmation of the fact that, independent of the character of the acid, the carrier of the color is actually the resonating cation of the structure of type (b).

However, upon dilution of the acids, as shown by our previous experiments [8], this type of cation hydrolyzes. Therefore, we conducted the given series of experiments with 10% hydrochloric acid as solvent. The results thus obtained are shown in Table 1, and are sketched graphically in Figs. 1, 2, 3 and

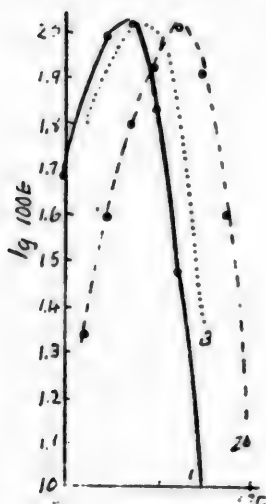


Fig. 1.

1-fuchsone; 2-benzaurin;
3-aurin

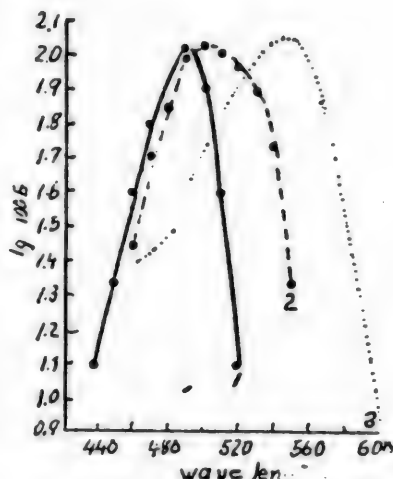


Fig. 2.

1-benzaurin; 2-monomethoxybenzaurin;
3-dimethoxybenzaurin.

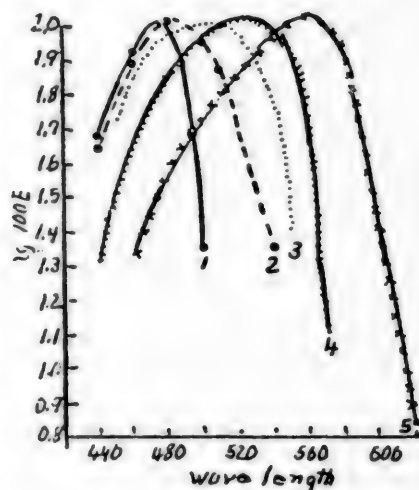


Fig. 3.

1-aurin; 2-monomethoxyaurin;
3-dimethoxyaurin; 4-trimethoxyaurin;
5-hexamethoxyaurin.

Fig. 1 gives a comparison of the absorption curves of hydrochloric acid solutions of fuchsone, benzaurin (hydroxyfuchsone) and aurin (dihydroxyfuchsone). These curves are similar in general character, but the hydroxyfuchsone dyes have a deeper color in mineral acid solutions than their chromogen. However, benzaurin, containing hydroxyls in the mesomeric form if the cation, is more deeply colored than aurin, which contains three hydroxyl groups: benzaurin gives an orange-yellow solution with mineral acids, aurin a yellow solution. In this case we can see a complete analogy to the basic dyes of the malachite green group and the crystal violet group, in which the former, containing two substituent amino groups, is more deeply colored than the latter, containing three such groups.

Table 1

Value of the quantity lg 100E in 10% hydrochloric acid

Name	fuchsone	methoxy fuchsone	benzaurin	methoxy benzaurin	dimethoxy-benzaurin	aurin	methoxy aurin	dimethoxy aurin	trimethoxy aurin	hexamethoxy aurin
Wave length	Concentration in moles/ $\underline{1 \cdot 10^{-6}}$									
	19	35	22	29	23	14	15	18	20	75
440	1.69	-	1.12	-	-	1.67	1.65	-	1.31	-
450	-	1.78	1.34	-	-	-	-	1.72	-	-
460	1.99	1.87	1.60	1.45	1.40	1.92	1.89	1.85	1.66	1.34
470	2.02	1.92	1.80	1.71	-	2.01	1.97	1.93	-	-
480	1.83	1.97	1.92	1.87	1.47	2.00	2.01	1.97	1.85	1.58
490	1.48	2.00	2.02	1.99	1.58	1.84	2.00	1.99	1.92	-
500	1.03	2.02	1.91	2.03	1.72	1.35	1.95	2.00	1.97	1.72
510	-	1.99	1.60	2.01	1.83	-	1.87	2.01	1.99	1.80
520	-	1.92	1.10	1.97	1.92	-	1.70	1.98	2.01	1.85
530	-	-	-	1.89	2.00	-	-	1.91	2.02	1.91
540	-	1.73	-	1.75	2.04	-	1.35	1.79	1.98	1.97
550	-	-	-	1.33	2.04	-	1.10	1.39	1.90	2.01
560	-	1.44	-	0.74	1.94	-	0.82	-	1.73	2.03
570	-	-	-	-	-	-	-	1.10	1.10	2.01
580	-	1.07	-	-	1.53	-	-	0.82	0.91	1.90
590	-	-	-	-	-	-	-	-	-	1.68
600	-	-	-	-	0.98	-	-	-	-	1.41
610	-	-	-	-	-	-	-	-	-	1.15
620	-	-	-	-	-	-	-	-	-	0.84

Upon introduction into fuchsone, benzaurin, or aurin of methoxy groups in positions ortho to the oxo or hydroxy groups, the color is very much deepened. In Fig. 2, the absorption curves of aurin and its mono- and dimethoxy derivatives in hydrochloric acid solution are compared.

An analogous influence is shown by methoxy groups in the aurin series; this can be seen from Fig. 3, in which are shown the comparative absorption curves of aurin and its mono-, di-, tri-, and hexamethoxy derivatives.

This bathochromic influence of the methoxyl groups has long been noted in the series of substantive azo dyes (Benzopurpurin 10B and Congo Red) and in the series of ice dyes; this investigation also confirms the bathochromic effect of the methoxyl group in the series of methylene quinone dyes.

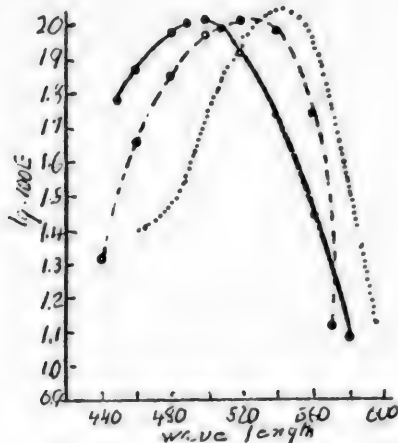


Fig. 4.

1-methoxyfuchsone;
2-dimethoxy benzaurin;
3-trimethoxyaurin

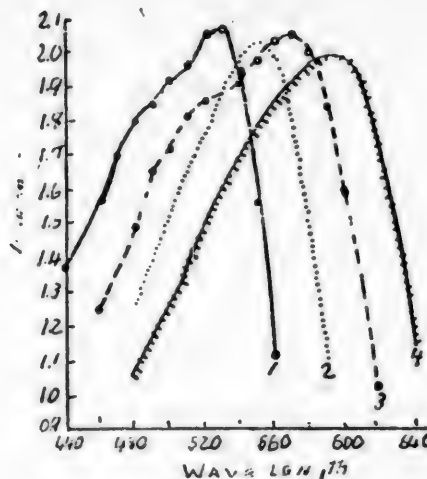


Fig. 5

1-aurin; 2-benzaurin; 3-trimethoxy
aurin; 4-dimethoxybenzaurin.

In addition, our data show that, like benzaurin, whose solutions in mineral acids are more deeply colored than the aurin solutions, the methoxy derivatives of benzaurin are also more deeply colored than the corresponding aurin derivatives. This can be seen from Fig. 4, which compares the absorption spectra of methoxy fuchsone, dimethoxybenzaurin, and trimethoxyaurin.

At the same time as we investigated the colors of solutions of hydroxyfuchsone dyes in mineral acid, we studied the color of their solutions in aqueous alkali. The carrier of the color in this case is the mesomeric anion (c), formed by dissociation of the hydroxyfuchsone form (a). However, in the presence of strong alkalis [9], this colored anion (c) adds the hydroxy group to its

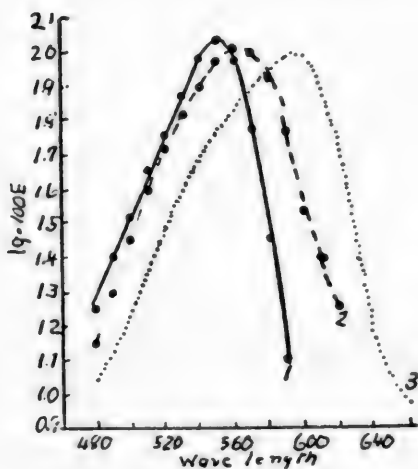


Fig. 6.

1-benzaurin; 2-monomethoxy-
benzaurin; 3-dimethoxybenzaurin.

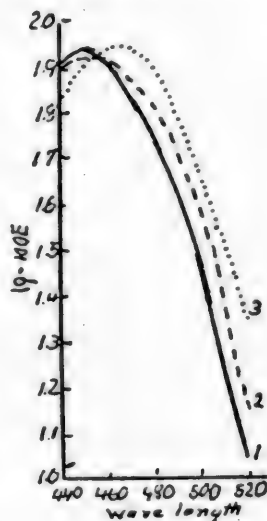


Fig. 9

1-benzaurin; 2-mono-
methoxybenzaurin;
3-dimethoxybenzaurin

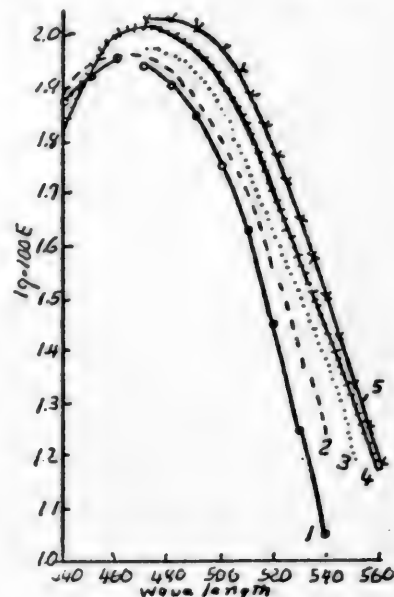


Fig. 10

1-aurin; 2-monomethoxyaurin;
3-dimethoxyaurin; 4-tri-
methoxyaurin; 5-hexamethoxy-
aurin

Table 2

Name	benzaurin	methoxy benzaurin	dimethoxy benzaurin	aurin	methoxy aurin	dimethoxy aurin	trimethoxy aurin	hexamethoxy aurin
Wave length	Concentration in moles/ 1 10 ⁻⁶							
	5	33	15	45	18	15	14	10
440	—	—	—	1.37	—	—	—	—
450	—	—	—	—	—	—	0.90	—
460	0.79	0.77	0.75	1.57	1.55	1.46	1.25	0.83
470	—	—	—	1.70	—	—	—	—
480	1.25	1.15	1.05	1.80	1.78	1.68	1.48	1.02
490	—	—	—	1.85	1.83	1.77	1.60	—
500	1.53	1.45	1.25	1.92	1.85	1.83	1.71	1.43
510	1.66	1.62	—	1.96	1.88	1.86	1.81	—
520	1.76	1.72	1.49	2.05	1.95	1.90	1.85	1.58
530	1.88	1.83	1.59	2.07	2.01	1.96	1.88	—
540	1.98	1.90	1.68	1.90	2.06	2.00	1.95	1.75
550	2.03	1.97	1.77	1.56	2.04	2.04	1.97	1.80
560	1.98	2.01	1.84	1.17	1.94	2.05	2.04	1.83
570	1.77	2.00	1.90	—	1.73	2.00	2.05	1.86
580	1.46	1.92	1.95	—	1.43	1.78	2.00	1.93
590	1.10	1.77	1.99	—	1.08	—	1.84	1.99
600	0.56	1.53	1.98	—	—	1.37	1.59	2.04
610	—	—	1.87	—	—	1.08	1.32	2.06
620	—	1.31	1.69	—	—	—	1.01	2.00
630	—	—	1.43	—	—	—	0.80	1.85
640	—	—	1.15	—	—	—	—	1.62
650	—	—	—	—	—	—	—	1.37
660	—	—	0.96	—	—	—	—	0.93

In Fig. 6, the absorption curves of alkaline solutions of benzaurin and its monomethoxy and dimethoxy derivatives are compared. In alkaline solutions too, the methoxy groups exhibit a strong bathochromic effect.

Analogous conclusions may be reached from a comparison of the absorption curves of aurin and its methoxy derivatives; these curves are sketched in Fig. 7. As is obvious from this figure, all the curves have a very similar character, with a single obvious maximum and with a definite bend in the left branch of the curve.

In Fig. 5 there is a comparison, on the one hand, of benzaurin and aurin, and on the other, of dimethoxy benzaurin and trimethoxy aurin. It is clear from this comparison that in alkaline solutions too, the dyes of the benzaurin group are more deeply colored than the corresponding dyes of the aurin group. The solutions of dimethoxy benzaurin are already colored blue.

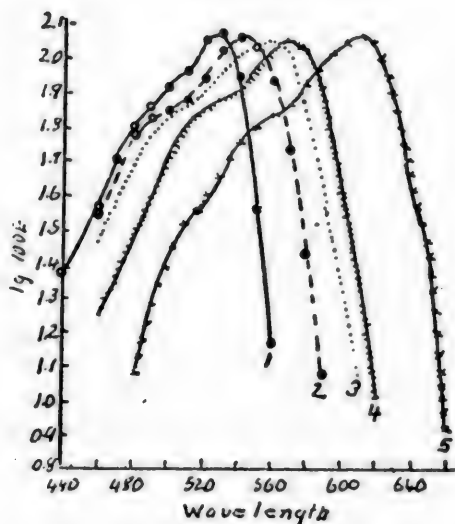


Fig. 7

1-aurin; 2-monomethoxy aurin;
3-dimethoxyaurin; 4-trimethoxyaurin;
5-hexamethoxyaurin.

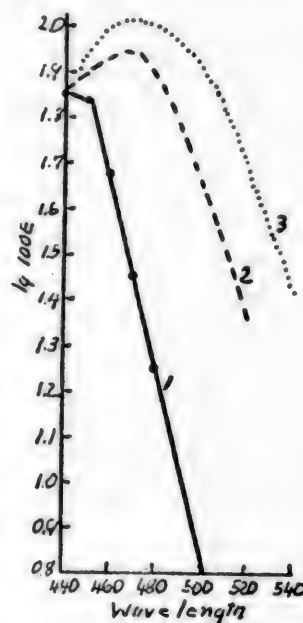


Fig. 8

1-methoxy fuchsons;
2-dimethoxy benzaurin;
3-trimethoxyaurin.

To complete the picture, we decided to compare the colors of the substances studied in neutral solution as well, in which these substances exist in unionized fuchsons or hydroxyfuchsons form. Fuchsons and methoxyfuchsons solutions, as well as the hydroxyfuchsons dyes in alcohol, are colored a weak yellow, and to the eye have very similar colors. None the less, a spectrophotometric comparison showed that the absorption spectra of the substances in question in their hydroxyfuchsons form exhibit the same differences, although not so noticeably, as in the ionized form, whether the latter exists in acid or in alkaline solutions. The results of experiments in this series are given in Table 3 and are shown graphically in Figs. 8, 9 and 10.

In Fig. 8, the absorption curves of methoxyfuchsons, dimethoxybenzaurin, and trimethoxyaurin, are compared. It is clear from this comparison that even in unionized condition, the hydroxyfuchsons dyes are colored somewhat more deeply than the fuchsons, which do not contain hydroxyl groups. However, in unionized

Table 3
Values of the quantity $\lg 100E$ in alcoholic solutions

Name	fuchsone	methoxy- fuchsone	benzaurin	methoxy- benzaurin	dimethoxy- benzaurin	aurin	methoxy aurin	dimethoxy aurin	trimethoxy aurin	hexamethoxy aurin
Wave length	concentration moles/l $\cdot 10^{-5}$									
	15	14	25	7	4	4	2	3	2	3
440	1.90	1.85	1.90	1.90	1.86	1.87	1.89	1.85	1.83	-
450	1.75	1.84	1.94	1.92	1.90	1.92	1.95	1.90	1.93	1.92
460	1.70	1.68	1.90	1.92	1.93	1.95	1.96	1.93	2.00	1.99
470	1.49	1.45	1.84	1.88	1.94	1.94	1.95	1.96	2.01	2.01
480	1.26	1.25	1.74	1.80	1.88	1.90	1.93	1.95	2.00	2.04
490	0.94	-	1.63	1.70	1.78	1.84	1.88	1.93	1.97	2.01
500	0.85	0.62	1.42	1.51	1.66	1.75	1.80	1.84	1.91	1.97
510	-	-	-	-	-	1.63	1.69	1.73	-	-
520	-	-	1.05	1.15	1.35	1.45	1.56	1.60	1.68	1.76
530	-	-	-	-	-	-	-	-	-	-
540	-	-	-	-	-	1.05	1.24	1.37	1.41	1.51
550	-	-	-	-	-	-	-	-	-	-
560	-	-	-	-	-	-	-	-	1.16	1.17
570	-	-	-	-	-	-	-	-	-	-

condition, the dyes of the benzaurin group are not colored noticeably deeper than the dyes of the aurin group.

In Figs. 9 and 10 is shown the influence of the methoxy groups on the color of hydroxyfuchsone dyes in unionized hydroxyfuchsone form. From these figures it is clear that the absorption curves of benzaurin and its methoxy derivatives as well as of aurin and its derivatives are very similar and that the introduction of methoxyl groups only very slightly, although still in accordance with the rules, shifts the maximum of absorption of the dyes.

SUMMARY

A comparison of the structure and color-producing properties of fuchsone and methoxyfuchsone, of benzaurin and its methoxy derivatives, and of aurin and its methoxy derivatives, containing one or several methoxy groups in the ortho position to the oxo group or hydroxy group, shows that:

1. Fuchsone and its hydroxy derivatives in unionized hydroxyfuchsone form give visually similar colored solutions; the absorption curves in the visible region of the spectrum are very similar, but the introduction of hydroxy and methoxy groups does produce, even though slightly, a bathochromic shift of the absorption maximum in accordance with the rules.

2. A hydroxyfuchsone dye in mineral acid solution gives exactly the same absorption curve, independent of the nature of the acid; this is a confirmation of the fact that the carrier of the color in mineral acid solutions is the mesomeric form of the cation, formed as a result of the addition of a proton to the dye in its hydroxyfuchsone form.

3. Just as the dyes of the malachite green group are more deeply colored than the corresponding dyes of the crystal violet group, the dyes of the benzaurin group in both mineral acid and alkaline solution are more deeply colored than the corresponding dyes of the aurin group.

4. The absorption curves of benzaurin and its methoxy derivatives are very similar in character (both in mineral acid and in alkaline solution), but the introduction of the methoxy groups has a bathochromic effect; the methoxy groups in the aurin series show a similar influence.

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Received February 23, 1948

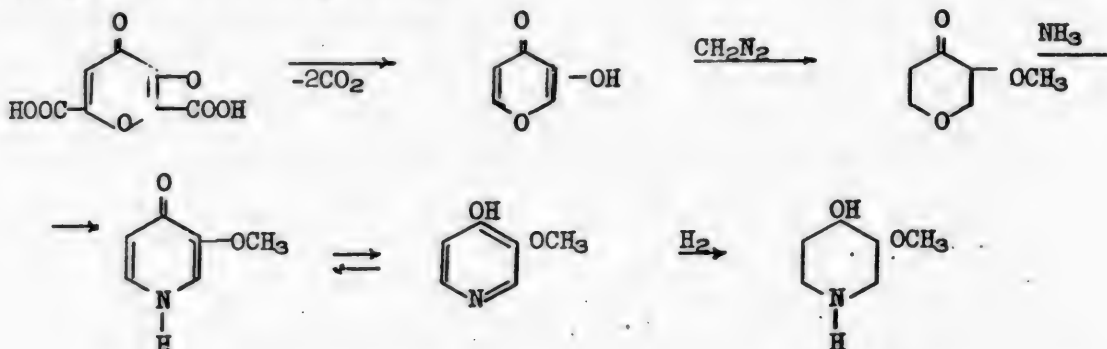
See CB translation p. 897 ff.

4-HYDROXY-3-METHOXY PIPERIDINE

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We have synthesized 4-hydroxy-3-methoxy piperidine from meconic acid according to the following scheme:



As a result of the decarboxylation of meconic acid by heating it with oxidized copper filings [1], β -hydroxy- γ -pyrone was obtained; this was converted by the action of diazomethane into β -methoxypyrone [2]. We observed that this β -methoxypyrone melted higher than was indicated by Peratoner and Spallino (94° instead of 85°). The explanation of this contradiction is apparently that the original β -hydroxypyrone (m.p. 116-118°) and β -methoxypyrone are very similar in their solubility and other properties, and that Peratoner and Spallino used a clearly insufficient quantity of diazomethane to methylate their β -hydroxypyrone (0.4 g CH_2N_2 instead of the theoretically calculated amount of 0.54 g).

Upon heating with aqueous ammonia, the β -methoxypyrone was converted into 4-hydroxy-3-methoxy pyridine [3], which was then reduced to 4-hydroxy-3-methoxy piperidine by sodium in absolute alcohol. The substance was obtained as a colorless liquid with the characteristic unpleasant odor of piperidine derivatives, boiling at 116-117° (19 mm).

EXPERIMENTAL

β -Hydroxy- γ -pyrone. Hydroxy pyrone was obtained by the dry distillation of technical meconic acid, mixed with oxidized copper filings in the ratio 1:1. The distillate was dried in vacuum and the residue extracted with chloroform. After removal of the chloroform, the substance was recrystallized from alcohol. Needles with m.p. 116-118°. Yield 50% of theory.

β -Methoxy- γ -pyrone. To a suspension of 13 g of hydroxypyrone in 100 ml of absolute alcohol there was added with cooling a distilled solution of diazomethane in ether, obtained from 24 ml of nitrosomethylurethane in 180 ml of absolute alcohol and 45 ml of a 25% solution of caustic potash, in methyl alcohol. Nitrogen was given off, and the β -hydroxypyrone was observed to dissolve, with the separation of another precipitate, which was filtered off, and united with the precipitate obtained from the mother liquor after removal of the ether. The

combined precipitates were recrystallized from benzene. The substance had a very pleasant odor, reminiscent of the odor of vanillin; m.p. 87-93°. To complete the purification, the methoxypyrrone was recrystallized from alcohol, then dissolved in chloroform and precipitated by the addition of petroleum ether, and finally, again recrystallized from benzene: colorless, flat needles, with m.p. 94°.

18.496 mg substance: 38.510 mg CO₂; 7.870 mg H₂O.

Found %: C 56.78; H 4.76.

C₈H₆O₃. Calculated %: C 57.1; H 4.76.

4-Hydroxy-3-methoxy pyridine. A mixture of 9 g of the methoxypyrrone, 75 ml of a 25% solution of ammonia, and 75 ml of water was heated on a boiling water bath for 2 hours. The solution formed was evaporated to dryness on a water bath, and the residue recrystallized from water with animal charcoal. Colorless, needle-shaped crystals, containing three molecules of water of crystallization. M.p. 114-115°. The anhydrous compound melted at 174° - 175°. Yield, 8 g.

4-Hydroxy-3-methoxy piperidine. To a boiling solution of 22 g of 4-hydroxy-3-methoxy pyridine in 250 ml of absolute alcohol there was added as rapidly as possible 70 g of metallic sodium. At the end of the reaction, to ensure the complete solution of the sodium, another small amount of absolute alcohol was added. The solution was diluted with an equal volume of water, neutralized with hydrochloric acid, and evaporated to dryness on the water bath. The carefully dried precipitate, containing a large quantity of sodium chloride, was extracted several times with absolute alcohol, and the extract was treated with a solution of 10 g of caustic potash in absolute alcohol. The precipitate of potassium chloride which settled out was removed, and washed with absolute alcohol; the filtrate was subjected to a fractional distillation, at first at atmospheric pressure, and then in vacuum. After the distillation of the 105-140° fraction at 13 mm, unreacted 4-hydroxy-3-methoxy pyridine was observed in the residue; after recrystallization and dessication, this weighed 7.35 g.

The 4-hydroxy-3-methoxy piperidine was in the form of a colorless liquid with an unpleasant odor, characteristic of piperidine derivatives. Yield 9 g, b.p. 116-117° at 19 mm; 114-115° at 17-18 mm; d_4^{20} 1.0779.

3.150 mg substance: 0.304 ml N₂ (24°, 754.5 mm).

Found %: N 10.78.

C₈H₁₃O₂N. Calculated %: N 10.7.

SUMMARY

1. 4-Hydroxy-3-methoxy piperidine has been synthesized.
2. More correct constants have been determined for β -methoxy- γ -pyrrone.

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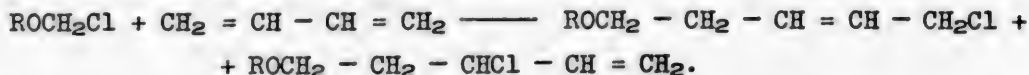
Received March 7, 1948.

THE ADDITION OF CHLORINE TO BUTADIENE AND THE REACTIONS OF THE ISOMERIC DICHLOROBUTENES.

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In a series of previous works, we studied the addition of several α -halogen ethers of the type $\text{CH}_2\text{Cl}-\text{O}-\text{R}$ (where $\text{R} = \text{CH}_3-$, C_2H_5- , $n\text{-C}_4\text{H}_9-$, $\text{iso-C}_4\text{H}_9-$) to butadiene in the presence of catalysts, and the various reactions of the addition products, the isomeric alkoxy chloropentenes.



In these studies we discovered the catalytic isomerization of the alkoxy chloropentene isomers [1], which were converted into halogen allyl isomers in the presence of zinc chloride and other metal halides; it was found that in determining the order of addition of halogen ethers to butadiene, in the sense of 1,2- and 1,4- addition, it was necessary to study the catalytic isomerization during the reaction of the addition products formed. Direct analysis of the final composition of the reaction mixture, even taking other similar cases into consideration, could not give a correct picture of the order of addition. Because of the catalytic isomerization of the isomeric alkoxy chloropentenes during the reaction, which was carried out with different amounts of catalyst and at different temperatures, it was found that α -chloromethyl ether, for instance, added to butadiene in the 1,2- position to the extent of 73-78%, and in the 1,4- position from 22-24%. A study of the catalytic isomerization of the isomeric alkoxy chloropentenes permitted us to draw some conclusions about the mechanism of the addition of α -halogen ethers to butadiene. We reached the conclusion that the addition did not take place ionically, i.e., according to Ingold's ionic mechanism, but that it was of the ionic-molecular or molecular type.

In continuing and developing this work, it appeared to us of interest and importance to study the addition to butadiene of other halogen-containing reagents, and first of all, addition of the halogens themselves, and the hydrogen halogen acids. In the present paper, we present the results obtained on the addition to butadiene of chlorine, and we describe the reactions of the isomeric dichlorobutenes chiefly from the point of view of our study of allyl rearrangements.

I. The Addition of Chlorine to Butadiene

The first to make a thorough study of the addition of chlorine to butadiene were Muskat and Northrup [2]. They isolated two isomeric dichlorides, and two tetrachlorides of butadiene. In their work they showed that the amount of 1,2-addition product formed, the 1,2-dichlorobutene-3, is usually twice as great as the amount of 1,4-addition product, 1,4-dichlorobutene-2.

Petrov and Sopov [3], carrying the study of the chlorination of butadiene further, found on the other hand that the 1,4- addition product was formed in greater quantity than the 1,2-; their ratio in the mixture was 3:2.

Immediately after the completion of our present work, a paper by Klebansky, Sorokina, and Khavin [4] appeared on the polymerization of halobutadienes, and in

answer to them, a second paper by A.A. Petrov and N.P. Sopov [5]; the latter authors among other things, again considered the question of the order of addition of chlorine to butadiene. They asserted that the yields of the isomeric dichlorobutenes varies within wide limits, depending on the amount of chlorine passed into the reaction mixture. When the amount of chlorine passed through increased by less than three times, the ratio of the 1,4- to the 1,2 dichloropentene changed from 5:3 to 0.9:1, that is, by a factor of almost two.

The data obtained by us on the addition of chlorine differ in certain respects both from the results of Muskat and Northrup and from what has been found in the work of A.A. Petrov and N.P. Sopov.

We directed most of our attention during the study of the addition of chlorine to butadiene to the explanation of the influence of the velocity and amount of chlorine passed through upon the relative quantities of dichlorides and tetrachlorides that were formed, and upon the ratio of the isomeric dichlorides.

The chlorination of butadiene was carried out in chloroform solution at a temperature of from -10 to -15° . In a series of experiments, we determined, in contradiction to the results of Muskat and Northrup, that despite the presence in the reaction mixture of a large excess of butadiene, the tetrachloride was formed to the extent of 20 to 30% of the weight of dichlorides; in proportion as the concentration of butadiene in the reaction mixture was decreased, the amount of tetrachloride gradually increased.

It is interesting to note that during the chlorination of butadiene in the absence of a solvent, neither the dichloride nor the tetrachloride was formed at all; there was observed instead the partial polymerization of the butadiene. The polymer was a jellylike, viscous mass.

In all probability, the partial polymerization of butadiene also takes place during chlorination in solvents, as after distillation of the dichlorides and tetrachlorides from the reaction mixture, there remains in the residue a small amount of tar, containing only a small quantity of halogen.

The formation of butadiene polymers in the chlorination process is confirmed by the results of A.A. Petrov and N.P. Sopov, who found that the percentage of halogen in the residue containing the tetrachlorides is somewhat less than the theoretical amount calculated for pure tetrachlorides. In order to explain the influence of the amount of chlorine passed through the reaction mixture on the ratio of isomeric dichlorobutenes formed, the chlorination of the chloroform solution of butadiene was conducted for different lengths of time, until the attainment of a definite increase in weight.

Distillation of the chloroform and fractionation of the reaction mixture were carried out with a meter column packed with glass rings, or a good Widmer dephlegmator. It was found that the ratio of 1,2- to 1,4-dichloropentene in the reaction mixture, in so far as it depended on the amount of chlorine passed through, varied only within comparatively narrow limits. The content of 1,2-dichlorobutene-3 in the different experiments amounted to from 55-60% of the total weight of dichlorides.

During the chlorination of butadiene in ether and benzene solutions, the ratio of isomeric dichlorobutenes usually remained the same. A.A. Petrov and N.P. Sopov in their latest paper claim that the ratio of isomeric dichlorobutenes obtained by chlorinating butadiene depends greatly on the amount of chlorine passed through the reaction mixture; the more chlorine passed through, the less 1,4-dichlorobutene is formed, and the more 1,2-dichlorobutene. Such a difference in the yields of the isomeric dichlorobutenes, depending upon the amount of chlorine passed through, might be expected, from our point of view, to exist only if there

were a difference in the velocity of addition of the chlorine to the isomeric dichlorobutenes formed in the reaction.

In order to clear up this question, we set up experiments on the chlorination of the isomeric dichlorobutenes under conditions similar to those of the chlorination of butadiene. A current of chlorine from a gasometer was passed through a chloroform solution of dichlorobutene which had been cooled to -15° , at such speed that a sixth of it was not absorbed. With the same quantity of isomeric dichlorides, and under the same conditions, the same volume of chlorine was passed through at the same time. After distillation of the chloroform, the amount of dichloride which had not reacted and the amount of tetrachlorides formed were determined. It was found that the addition of chlorine to the isomeric dichlorobutenes takes place at practically the same speed. During the addition of chlorine to the 1,4-dichlorobutene, a solid tetrachloride and a very small amount of liquid tetrachloride are formed, and during the addition to the 1,2-dichlorobutene, a mixture consisting of 50 to 56% of liquid and 44 to 50% of solid tetrachlorides is formed.

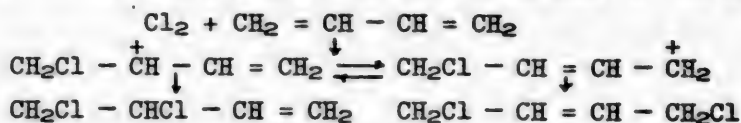
The results of these experiments have a great deal of significance also in considering the order of addition of chlorine to butadiene. On them we can base the conclusion that the secondary reaction of chlorine addition to the isomeric dichlorobutenes, taking place at practically the same speed, does not vary with the proportions of dichlorobutenes in the reaction mixture during chlorination, and that, consequently, the order of addition of chlorine to butadiene may be determined by direct analysis of the final reaction mixture. The characterization of the addition of chlorine to butadiene, however, can not be considered complete, if we do not consider also the possibility of isomerization of the dichlorobutenes formed during the reaction, separation, and purification, for it is known that the halogen allyl isomers, under definite conditions, may easily be transformed into each other. The possibility of catalytic isomerization of the dichlorobutenes during the reaction is excluded, as the chlorination of the butadiene was carried out in the absence of a catalyst.

The possibility of thermal isomerization of the dichlorobutenes, generally speaking, cannot be excluded a priori, as during their distillation from the reaction mixture and purification by fractionation, they are heated up to $100-120^{\circ}$.

Experiments on the study of thermal isomerization of the isomeric dichlorobutenes have shown their exceptional stability; isomerization practically does not take place during the heating of the 1,2- and 1,4-dichlorobutenes at 120° for a lengthy period. Upon heating 1,2-dichlorobutene in a sealed tube at 200° for 10 hours, it was isomerized to the extent of 8%. From these figures, we may draw the conclusion that the thermal isomerization of the isomeric dichlorobutenes does not take place during the reaction, separation, and purification.

As for the mechanism of the addition of chlorine to butadiene, we have omitted any review of earlier theories, and have attempted to explain the addition of reagents to conjugated systems chiefly by means of the theory of partial valences. We shall here dwell only upon the latest scheme, put forth by Muskat and Northrup.

To explain the mechanism of the addition of chlorine to butadiene, Muskat and Northrup accept the well-known ionic theory of Ingold [6], assuming that the process of addition takes place ionically according to the scheme:



The formation of similar ionic structures is also accepted in modern resonance theory, [7].

A study of the addition of α -halogen ethers to butadiene and the catalytic isomerization of the addition products, conducted by us previously, has shown, however, the impossibility of accepting completely the above scheme for describing the addition process.

To explain the mechanism of the addition of chlorine to butadiene, we

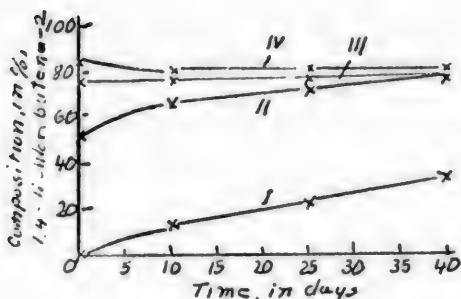


Fig. 1

studied the catalytic isomerization of the dichlorobutenes. The study of the question also has an independent interest. Isomerization was carried out in the presence of zinc chloride at 17°. The experiments showed that the velocity of isomerization of the isomeric dichlorobutenes was fall smaller than the velocity of the isomeric alkoxy chloropentenes. Obviously, the CH_2Cl group has a much smaller inductive effect than groups of the type ROCH_2- and $-\text{CH}_2$; as a consequence, the mobility of the halogen in the dihalobutenes is decreased. The results obtained on catalytic isomerization of the isomeric dichlorobutenes and their mixtures are shown in the figure. As is evident from it, the equilibrium mixture of dichlorobutenes consists of 67-70% of 1,4- and 30,33% of the 1,2-dichlorobutene.

On the basis of a study of the behavior of the complexes of halogen alkyls with aluminum chloride and other metal halides which play an important role in the Friedel-Crafts reaction, a majority of the investigators [8] believe that they have an ionic character. In order to explain the mechanism of catalytic and thermal isomerization of halo-allyl isomers, an exclusively ionic mechanism may also be acceptable. The ionic mechanism of isomerization of the ester of p-nitrobenzoic acid with phenyl allyl alcohol has been shown experimentally by Burton [9].

From a comparison of the ratio of 1,2- to 1,4-dichlorobutene, found as a result of the addition of chlorine to butadiene, and the ratio at equilibrium during the catalytic isomerization of the dichlorobutenes, it is obvious that the difference existing here (25%) is beyond any possible error of the experiments. This difference, in our opinion, can be explained by the fact that the addition of chlorine to butadiene takes place not only ionically, but partly as a molecular reaction, during which the polarization of the halogen atoms in the molecule at the moment of addition does not reach the point of complete ionization. A final decision of this question on the basis of experimental data available at present, however, is not possible.

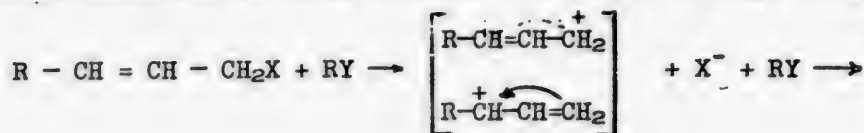
II. Reactions of the Isomeric Dichlorobutenes

As has been shown by the investigations of Meisenheimer and Link [10], the American school of Young [11], and our own investigations [12], all the reactions of the haloid allyl compounds with different reagents may be divided into three groups.

1. The normal reaction of double interchange, taking place according to the bimolecular type and leading to the formation of products without rearrangement (S_{N}^2 type):



2. Reactions taking place according to the monomolecular type with the formation of resonant bound carbon ions, leading to mixtures of allyl isomers (S_N^1 type):



3. Reactions taking place bimolecularly with internal rearrangement, leading to the formation of products of isomeric structure:



As our previous investigations have shown, the reactions of the isomeric methoxy and butoxychloropentenes with various reagents (acetates of the alkaline metals, aqueous and alcoholic alkali, sodium hydrosulfide, magnesium organic compounds, sodium and magnesium acetoacetic and malonic esters, sodium diethyl phosphite and the complete esters of phosphorous acid) take place according to both the first and second types, as well as according to mixed first and second types.

In connection with the study of these reactions, there is a special interest in the study of the reactions of the isomeric dichlorobutenes, both from the point of view of confirming the conclusions drawn in previous research, and from the point of view of their special theoretical importance.

The action of potassium acetate, and of aqueous and alcoholic alkali solutions upon the isomeric dichlorobutenes was studied, as well as the reactions of the latter with sodium diethyl phosphite and triethyl phosphite.

In carrying out the reactions between 1,4-dichlorobutene-2 and potassium acetate in acetic acid solution, we obtained a mixture of acetates, consisting of 91.5% of the acetate of butene-2-diol-1,4 (b.p. 116° at 12 mm, n_D^{20} 1.4435; d_4^{20} 1.0826) and 8.5% of the acetate of butene-3-diol-1,2 (b.p. 86° - 88° at 10 mm, n_D^{20} 1.4305; d_4^{20} 1.0603). The total yield of acetates amounted to 96% of theory.

Under the action of potassium acetate, 1,2-dichlorobutene-3 gave a mixture of acetates, consisting of 35% of the acetate of butene-2-diol-1,4 and 65% of the acetate of butene-3-diol-1,2. It is of interest to note that the reaction of 1,2-dichlorobutene-3 with sodium acetate, when the experiment was carried out in the same way, practically did not take place.

The ratios of acetates obtained from the isomeric dichlorobutenes and those obtained from the isomeric methoxychloropentenes (92% and 8% from the first and 62% and 38% from the second) were very close. We may conclude, by analogy with the reactions of the methoxychloropentenes, that 1,4-dichlorobutene-2 reacts chiefly according to the S_N^2 type and partially according to the S_N^1 type; 1,2-dichlorobutene-3 reacts completely according to the S_N^1 type.

Obviously, the CH_2Cl group lowers the mobility of the halogen in the halo-allyl system by comparison with the $ROCH_2CH_2$ group, but has little influence on the ratio of the S_N^2 and S_N^1 reactions and the ratio of isomers formed according to the S_N^1 type reaction.

Upon saponification of the 1,4-dichlorobutene-2 salt in aqueous solution, a mixture of the diols was obtained, consisting of 76% butene-2-diol-1,4 and 24% of butene-3-diol-1,2. The ratio of isomeric diols obtained is fairly close to the ratio of isomeric pentenols (71% and 29%) obtained by the saponification of 1-methoxy-5-chloropentene-3.

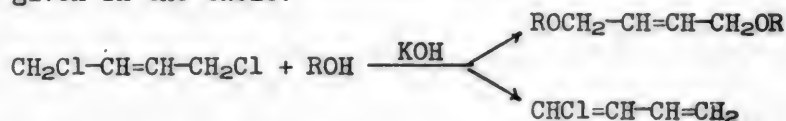
Saponification of 1,2-dichlorobutene-3 under similar conditions practically did not take place. An increase of the period of heating to 120 hours, along with very intensive stirring also did not lead to the formation of products of saponification. The greater part of the original dichloride was recovered.

The slowness of the tendency of 1,2-dichlorobutene-3 to react in comparison with the reactivity of the alkoxychloropentenes may be explained from the point of view of resonance theory [13]. In 1,2-dichlorobutene-3, the resonance of the π electrons of the two halogen atoms is impossible. Resonance of the C-Cl bond with an ionic condition is possible only for a single bond, as in this case both carbon atoms must carry a positive charge. Because of this, the weight of the ionic condition in the C-Cl bond of 1,2-dichlorobutene-3 is less than in the usual C-Cl bond; this is also a cause of the decrease in the reactivity of the halogen atoms.

The action of alcoholic alkali upon halo-allyl isomers has been described by us in previous communications [14]. It has been shown that in the passage from methyl to ethyl, propyl, n-butyl, and tertiary butyl alcohol, as a result of the decrease in dissociation of these alcohols into an alkoxy ion and a proton, the bimolecular S_N^2 reaction (the formation of ethers) is decreased, and the monomolecular S_N^1 (formation of the isomeric chloride) is increased.

In order to broaden our generalization about these reactions still further, we studied the action of alcoholic alkali on the isomeric dichlorobutenes.

Under the action of KOH upon 1,4-dichlorobutene-2 in a solution of methyl alcohol, only a single product is formed - the dimethyl ether of butene-2-diol-1,4. In propyl and n-butyl alcohols, in addition to the corresponding diethers, a small quantity of the α -chlorobutadiene is formed. The constants of the diethers are given in the table.



In tertiary butyl alcohol, the chief reaction is the formation of α -chlorobutadiene.

Formula	Boiling point	n_D^{20}	d_4^{20}
$\text{CH}_3\text{OCH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{OCH}_3$	142° (760 mm)	1.4210	0.8967
$n\text{-C}_3\text{H}_7\text{OCH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{OC}_3\text{H}_7$	83° (9 mm)	1.4310	0.8631
$n\text{-C}_4\text{H}_9\text{OCH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{OC}_4\text{H}_9$	98-100° (5 mm)	1.4365	0.8618

Under the action of KOH upon 1,2-dichlorobutene-3 both in the absence of a solvent and in solutions of alcohols, the splitting off of a single molecule of hydrogen chloride takes place with the formation of chloroprene.

Attention may be drawn to the fact that under the action of alcoholic alkali, the 1,4- and 1,2-dichlorobutenes form structurally different halogen-substituted diene hydrocarbons. This may be explained by the fact that the splitting off of a molecule of hydrogen chloride from 1,4-dichlorobutene-2, or, more accurately, from its resonance form $\text{HCHCl}=\text{CH}-\text{CH}=\text{CH}_2$ [5] takes place with greater speed than its isomerization to 1,2-dichlorobutene-3, thanks to the lack of mobility of its halogen atoms.

The reaction of 1,4-dichlorobutene-2 with sodium diethylphosphite gives a small yield of 1,4-di-diethylphosphonebutene-2, with b.p. 226° at 15 mm; n_D^{20} 1.4547; d_4^{20} 1.1247. The reaction of the sodium diethylphosphite with 1,2-dichlorobutene-3 leads to the formation of no definite products.

A further study was made of the reaction of 1,4-dichlorobutene-2 with triethylphosphite. The yield of 1,4-di-diethylphosphone butene-2 in this case reached 53%. The reaction takes place completely according to the S_N type, without the formation of an isomeric product.

The reaction of the 1,2-dichlorobutene-3 with triethyl phosphite leads chiefly to the formation of a solid, glassy polymer.

EXPERIMENTAL

The addition of chlorine to butadiene in chloroform solution. Experiment 1. In a round-bottomed liter flask fitted with a mechanical stirrer and a reflux condenser, were placed 200 g of chloroform and 200 g of technical butadiene, containing 90% butadiene. Then, with slow stirring and cooling with a refrigerant mixture, a current of dry chlorine was passed into the solution with a velocity of 2-3 bubbles per second. The chlorination was cut short when the increase in weight of the flask reached 30 g. The chloroform was distilled off from the reaction mixture through a Widmer dephlegmator, at first at ordinary pressure, and then in vacuum under a residual pressure of 100 mm. After the chloroform had been removed, the butadiene dichloride was first distilled off, and then fractionated in a Widmer dephlegmator; for the complete removal of any 2,3-dichlorobutane, formed by the addition of chlorine to the pseudobutylene in the butadiene, it was finally fractionated in a meter column (diameter of inner tube 9 mm) filled with glass rings and fitted with a Whitmore type of condenser. There were thus obtained 10 g of 1,2-dichlorobutene-3 with b.p. 43°-44° at 44 mm; n_D^{20} 1.4605, and 8.2 g 1,4-dichlorobutene-2 with b.p. 75-76° at 40 mm; n_D^{20} 1.4888. The residue, containing tetrachloride, amounted to 8.1 g. Upon standing, crystals of tetrachloride precipitated from it. After recrystallization from chloroform, the crystals melted at 73°.

Experiment 2. The chlorination of butadiene was carried out under similar conditions until there was increase in weight of 65 g. Fractional distillation of the reaction mixture gave 36.3 g of 1,2-dichlorobutene-3 and 28 g of 1,4-dichlorobutene-2. The residue, containing tetrachloride, 31.5 g.

Experiment 3. The chlorination was carried out until the gain in weight was 180 g. 85 g of 1,2-dichlorobutene-3 was obtained, and 78 g of 1,4-dichlorobutene 2. The residue containing tetrachloride, 143 g.

Chlorination of butadiene in ether solution, benzene solution, and without a solvent. Experiment 1. To a solution of 200 g of butadiene and 400 ml of absolute ether, during cooling with a refrigerant mixture and mechanical stirring, a current of chlorine was passed in for 6 hours. The ether was distilled off through a Widmer dephlegmator, and the residue fractionated in vacuum with a residual pressure of 40 mm. There were obtained 44 g of the 1,2-dichloride and 40 g of the 1,4-dichloride.

Experiment 2. A current of chlorine was passed for 6 hours into a solution of 200 g of butadiene in 400 ml of benzene with cooling. The benzene was distilled off in vacuum under a residual pressure of 150 mm. After fractional distillation of the residue, 23 g of the 1,2-dichloride and 18.5 g of the 1,4-dichloride were obtained. Residue containing tetrachloride, 18.3 g.

Experiment 3. The chlorine was passed into 400 g of the butadiene, which

was kept cooled to -15° , at a velocity of 2 or 3 bubbles per second for 5 hours. The butadiene was distilled through a Widmer column. After all the butadiene had been distilled off, there remained in the flask a small quantity (15-20 g) of butadiene polymer in the form of a colorless, jellylike, viscous mass. No dichlorides or tetrachlorides of butadiene were observed.

The addition of chlorine to the isomeric dichlorobutenes. Experiment 1. Into a solution of 20 g of 1,4-dichlorobutene-2 in 40 ml of chloroform, during cooling with a refrigerant mixture, 3 liters of chlorine were passed in a period of 30 minutes. The velocity of the chlorine stream was regulated in such a way that $5/6$ of the chlorine passed in was absorbed. The chloroform was distilled off from the flask with a Widmer dephlegmator at atmospheric pressure. The residue was fractionated in a vacuum under a residual pressure of 40 mm. There were obtained 9 g of the original dichloride and 16 g of a fraction with b.p. $110-130^{\circ}$ at 40 mm. Upon standing, the fraction crystallized almost completely. After squeezing of the crystals, 0.6 g of liquid and 14.6 g of solid tetrachlorides were obtained.

Upon chlorination of the 1,2-dichlorobutene-3 under similar conditions, 8.5 g of the original chloride was obtained, along with 7.7 g of the solid, and 6.1 g of the liquid tetrachlorides.

Experiment 2. Three liters of chlorine were passed in the course of 30 minutes into a solution of 25 g of 1,4-dichlorobutene-2 in 30 ml of chloroform cooled with a refrigerant mixture. Fractional distillation of the reaction mixture gave 14 g of the original dichloride, 18.5 g of the solid, and 1.5 g of the liquid tetrachloride.

In a similar experiment with 1,2-dichlorobutene-3, 12.7 g of the original chloride was obtained, along with 8 g of the solid and 8.2 g of the liquid tetrachlorides.

Thermal and catalytic isomerization of 1,2-dichlorobutene-3. No isomerization was observed upon heating 1,2-dichlorobutene-3 and 1,4-dichlorobutene-2 in sealed ampoules at 130° for 5 hours. Upon heating 1,2-dichlorobutene-3 for 10 hours at 200° , the index of refraction of the chloride was changed from 1.4605 to 1.4620.

The catalytic isomerization of the isomeric dichlorides was studied at room temperature in the presence of 1% zinc chloride. The percent isomerization of the chlorides was calculated from the change in index of refraction of the mixtures. This convenient method of carrying out the isomerization has been described in our previous articles. Results obtained by isomerization of the pure dichlorobutenes and their mixtures are sketched in the figure. The equilibrium mixture consists of 30 to 33% of the 1,2- and 67 to 70% of the 1,4-dichlorobutene.

The action of potassium acetate on 1,4-dichlorobutene-2 in acetic acid solution. 15 g of 1,4-dichlorobutene-2, 20 g of glacial acetic acid, and 30 g of powdered potassium acetate were heated for 5 hours in an oil bath at a temperature of $130-140^{\circ}$. After cooling, the reaction mixture was diluted with water and extracted with ether. The ether extract was dried with calcium chloride, the ether distilled off, and the residue fractionated in vacuum in a flask with a spiral Widmer column. There was obtained 1.8 g of the acetate of butene-3-diol-1,2:

B.p. $86-88^{\circ}$ (10 mm); n_D^{20} 1.4305; d_4^{20} 1.0603.

Found: MR_D 41.94.

$C_8H_{12}O_4$. Calculated: MR_D 41.75

0.1660 g substance: 0.3418 g CO_2 ; 0.1058 g H_2O .

Found %: C 55.48; H 6.99.

$C_8H_{12}O_4$. Calculated %: C 55.81; H 6.91.

B.p. 116° (12 mm); n_D^{20} 1.4435; d_4^{20} 1.0826

Found: MR_D 42.12.

$C_8H_{12}O_4F$. Calculated: MR_D 41.75.

0.1736 g substance: 0.3418 g CO_2 ; 0.1032 g H_2O .

Found %: C 55.96; H 6.61.

$C_8H_{12}O_4$. Calculated %: C 55.81; H 6.91.

The action of potassium acetate on 1,2-dichlorobutene-3 in acetic acid solution. 15 g of 1,2-dichlorobutene-3, 20 g of glacial acetic acid, and 30 g of powdered freshly melted potassium acetate were heated for 5 hours in an oil bath at a temperature of 130°-140°. Upon treatment and fractional distillation of the reaction mixture, there were obtained 6.1 g of the acetate of butene-3-diol-1,2 with b.p. 86-87° (10 mm); n_D^{20} 1.4310 and 3.3 g of the acetate of butene-2-diol-1,4 with b.p. 114° (10 mm); n_D^{20} 1.4430.

Saponification of 1,4-dichlorobutene-2. 64 g of calcined soda was dissolved in 430 g of water, and to the solution obtained, 50 g of 1,4-dichlorobutene-2 was added. The reaction mixture was heated on a boiling water bath for 16 hours.* Most of the water was then distilled off in a flask with a Widmer dephlegmator, and the remainder filtered from the precipitated residue of sodium chloride. The residue on the filter was washed with ether. After the ether was driven off, the residue was united with the aqueous filtrate. By fractionation of the filtrate, 9.2 g of butene-3-diol-1,2 was obtained:

B.p. 95° (13 mm); n_D^{20} 1.4616; d_4^{20} 1.0466.

Found: MR_D 23.01.

$C_4H_8O_2F$. Calculated: MR_D 23.25.

0.1451 g substance: 0.2890 g CO_2 ; 0.1190 g H_2O .

Found %: C 54.32; H 9.11.

$C_4H_8O_2$. Calculated %: C 54.54; H 9.09.

and 9.9 g of butene-2-diol-1,4:

B.p. 132° (13 mm); n_D^{20} 1.1467; d_4^{20} 1.0800.

Found: MR_D 23.10.

$C_4H_8O_2F$. Calculated: MR_D 23.25.

0.1856 g substance: 0.3717 g CO_2 ; 0.1505 g H_2O .

Found %: C 54.62; H 9.01.

$C_4H_8O_2$. Calculated %: C 54.54; H 9.09.

Saponification of 1,2-dichlorobutene-3. The saponification of 1,2-dichlorobutene-3 was carried out under conditions similar to those described in the previous experiment. For the reaction, 50 g of 1,2-dichlorobutene-3 and 100 g of calcined soda were taken. The reaction was carried out with very intensive stirring of the reaction mixture. After 120 hours of heating, a layer of unchanged chloride still remained on the surface of the solution. The layer was separated, dried, and distilled. B.p. 41-44° (40 mm); n_D^{20} 1.4625. No butene diols were obtained as products of saponification from the aqueous layer.

The action of KOH on 1,4-dichlorobutene-2 in a solution of methyl alcohol. 20 g of KOH was dissolved in 100 g of methyl alcohol, and to the solution obtained 20 g of 1,4-dichlorobutene-2 was added. The mixture was heated for 3 hours on a water bath. The alcohol was then distilled off, and the residue diluted with water, and extracted with ether. After removal of the ether by distillation, the residue was fractionated in vacuum. There was obtained 7.7 g of the dimethyl ether of butene-2-diol-1,4:

*With intensive mechanical stirring.

B.p. 142° (760 mm); n_D^{20} 1.4210; d_4^{20} 0.8967.

Found: MR_D 32.80.

$C_8H_{12}O_2F$. Calculated: MR_D 32.73.

0.097 g substance: 0.2200 g CO_2 ; 0.0930 g H_2O .

Found %: C 61.86; H 10.65.

$C_8H_{12}O_2$. Calculated %: C 62.07; H 10.34.

Oxidation of the dimethyl ether of butene-2-diol-1,4 with potassium permanganate. 4 g of the product was dissolved in 300 ml of water, and then, gradually, with continuous shaking, 15 g of powdered potassium permanganate was added. During the oxidation, the temperature of the solution did not rise above 20°. After a day's standing, the solution above the precipitate of manganese dioxide became transparent. The manganese dioxide was filtered off and washed on the filter with hot water. The filtrate was evaporated almost to dryness, and the residue treated with dilute hydrochloric acid. The solution obtained was extracted several times with ether, the ether extract was dried with calcium chloride, the ether was distilled off, and the residue fractionated in vacuum. There was obtained 2.7 g of methoxyacetic acid, with b.p. 92° at 9 mm; n_D^{20} 1.1170.

Action of KOH on 1,4-dichlorobutene-2 in a solution of propyl alcohol. 20 g of KOH was dissolved in 100 g of propyl alcohol with heating, and to the solution obtained was added 15 g of 1,4-dichlorobutene-2. The reaction mixture was heated for 3 hours on a water bath. The propyl alcohol was then distilled off from the reaction mixture through a Widmer dephlegmator. The first fractions of propyl alcohol amounting to 10 ml were collected separately, treated with water, extracted with ether, and distilled. There was obtained about 3 g of a fraction with b.p. 63-85°. This fraction was again treated with water and extracted with ether. Distillation of the ether extract gave 0.4 g of α -chlorobutadiene with b.p. 65-66° (760 mm). The residue was fractionated in vacuum. There was obtained 7.1 g of the dipropyl ether of butene-2-diol-1,4:

B.p. 83° (9 mm); n_D^{20} 1.4310; d_4^{20} 0.8631.

Found: MR_D 51.59.

$C_{10}H_{20}O_2F$. Calculated: MR_D 51.20.

0.0978 g substance: 0.2498 g CO_2 ; 0.1050 g H_2O .

Found %: C 69.66; H 11.93.

$C_{10}H_{20}O_2$. Calculated %: C 69.76; H 11.62.

Action of KOH on 1,4-dichlorobutene-2 in a solution of n-butyl alcohol. To a solution of 25 g of KOH in 150 g of n-butyl alcohol, 20 g of 1,4-dichlorobutene-2 was added. The reaction mixture was heated for 3 hours on a water bath. The butyl alcohol was distilled off through a Widmer dephlegmator. The first distillate of butyl alcohol with b.p. 100-115° was collected separately, and treated with water and ether, as described in the preceding experiment. There was obtained 0.7 g of a substance with b.p. 66° (760 mm) and n_D^{20} 1.4660. Pure chlorobutadiene, according to the data of A.A. Petrov and N.P. Sopov, has a b.p. of 65.5-66°, n_D^{20} 1.4720. Obviously, the α -chlorobutadiene obtained by us was contaminated with ether and n-butyl alcohol, which lowered the index of refraction of the α -chlorobutadiene.

After the removal of the n-butyl alcohol from the reaction mixture by distillation, the residue was treated with water until the precipitate of potassium chloride dissolved; the solution was extracted many times with ether. The ether extract was dried over calcium chloride, the ether distilled off, and the residue fractionated in vacuum. There was obtained 7.3 g of the di-n-butyl ether of butene-2-diol-1,4:

The residue was treated with water and extracted with ether, dried and the ether distilled off.

B.p. 98-100° (5 mm); n_D^{20} 1.4365; d_4^{20} 0.8618.

Found: MR_D 60.73.

$C_{12}H_{24}O_2$ F. Calculated: MR_D 60.44.

0.1006 g substance: 0.2640 g CO_2 ; 0.1062 g H_2O .

Found %: C 71.57; H 11.73.

$C_{12}H_{24}O_2$. Calculated %: C 72.00; H 12.00.

Action of KOH on 1,4-dichlorobutene-2 in a solution of tert. butyl alcohol.
To a solution of 20 g of KOH in 120 g of tert butyl alcohol there was added 15 g of 1,4-dichlorobutene-2. The mixture was heated on a water bath for three hours. During the removal of the tert. butyl alcohol by distillation, the first fraction with b.p. up to 81° was collected separately. After it had been treated with water and ether, and fractionated from a small round-bottomed flask, it gave 4.7 g of a substance with b.p. 64-66° (760 mm) and n_D^{20} 1.4650. The chlorobutadiene obtained contained some ether and possibly tert. butyl alcohol; in consequence, the index of refraction was low.

After all the tert. butyl alcohol had been distilled off from the reaction mixture, the residue was treated with water and ether. The ether was distilled off, and the residue fractionated in vacuum. A fraction was obtained with b.p. 40-80° (9 mm) and n_D^{20} 1.4456, to the amount of 4.3 g. A second fractionation of this fraction from a small flask with a Widmer dephlegmator did not give a substance with a constant boiling point.

The action of KOH on 1,2-dichlorobutene-3 without a solvent, and in a solution of ethyl alcohol. Experiment 1. 12 g of 1,2-dichlorobutene-3 and 12 g of powdered KOH were heated on a water bath. The reaction began quickly and took place in a very stormy manner. There was obtained 6 g of chloroprene, with b.p. 59° and n_D^{20} 1.4572.

Experiment 2. To a solution of 40 g of KOH in 200 ml of ethyl alcohol, there was added 30 g of 1,2-dichlorobutene-3. The reaction mixture was heated for 3 hours on the water bath. The ethyl alcohol was distilled off. The first fraction, with b.p. 55-70°, was treated with water. The layer which was separated from the water was dried and distilled. There was obtained 15.5 g of chloroprene, with b.p. 59°; n_D^{20} 1.4575.

Most of the ethyl alcohol was distilled off from the reaction mixture through an eight-bulbed dephlegmator of the A.E. Arbuzov type. The residue was treated with water and extracted with ether. The ether extract was dried over calcium chloride, the ether distilled off, and the residue fractionated in vacuum. There was obtained 1.2 g of a fraction with b.p. 150-165° (760 mm); n_D^{20} 1.4280; apparently this contained chiefly the diethyl ether of butene-3-diol-1,2, contaminated with other substances. Elementary analysis of the fraction gave a slightly lowered carbon and hydrogen content compared to the theoretical calculated for the diethyl ether of butene-3-diol-1,2.

Action of sodium diethyl phosphite on 1,4-dichlorobutene-2. To 6.7 g of sodium, placed under a layer of absolute ether, there was gradually added 40 g of diethylphosphorous acid. After all the sodium had been dissolved, 40 ml of absolute benzene was added, and 15 g of 1,4-dichlorobutene-2 was dropped in. The mixture evolved heat. After the ether had been distilled off, the reaction mixture was heated on a boiling water bath for 3 hours. After cooling, the solution was poured off from the precipitate of sodium chloride, the benzene distilled off in an oil bath, and the residue fractionated. After distillation of the partially unreacted dichloride and diethylphosphorous acid, 2.9 g of 1,4-di-diethylphosphone-butene-2 came over:

B.p. 226° (15 mm); n_D^{20} 1.4547; d_4^{20} 1.1247.
0.1182 g, 0.1775 g substance: NaOH used 22.6 ml; 34.1 ml ($T = 0.02085$).
Found %: P 18.68, 18.77.
 $C_{12}H_{26}O_3P_2$. Calculated %: P 18.90.

The residue from the fractionation was a viscous, glassy material with a yellow color.

The action of sodium diethylphosphite on 1,2-dichlorobutene-3. The proportions of the components and the conduct of the reaction were the same as in the preceding experiment. The reaction gave a thick, viscous, yellow mass, which could not be distilled in vacuum.

The action of the ethyl ester of phosphorous acid on 1,4-dichlorobutene-2. 7 g of 1,4-dichlorobutene-2 and 20 g of triethylphosphite were heated in a sealed tube at 200° for 10 hours. Fractional distillation of the reaction mixture gave 6.5 g of a fraction with b.p. 80-88° (16 mm); n_D^{20} 1.4240 and 9.6 g of 1,4-di-diethyl phosphonebutene-2 with b.p. 226° (15 mm); n_D^{20} 1.4547. The residue in the flask was 4.5 g; it was a solid, yellow, glassy mass.

Fractionation of the fraction with b.p. 80-88° (16 mm) gave about 3 g of the ethyl ether of ethylphosphinic acid. B.p. 87-88° (16 mm); n_D^{20} 1.4150.

The action of the ethyl ester of phosphorous acid on 1,2-dichlorobutene-3. The reaction was carried out in the manner described in the preceding experiment. It gave 8 g of the ethyl ester of ethyl phosphinic acid and a fraction with b.p. 120°-160° (16 mm); n_D^{20} 1.4300 to the amount of 2.5 g. The 10 g of residue was a solid, vitreous, tar.

SUMMARY

1. The addition of chlorine to butadiene in chloroform, ether, and benzene solution has been studied. In the mixture of isomeric dichlorobutenes, there is 55-60% of the 1,2-dichlorobutene-3. The ratio of dichlorobutenes formed is practically independent of the amount of chlorine passed through the reaction mixture.
2. During the chlorine-treatment of butadiene in the absence of solvents, partial polymerization takes place; no products of the addition of chlorine to butadiene were observed.
3. The addition of chlorine to the isomeric dichlorobutenes takes place at practically the same speed.
4. A small quantity of butadiene tetrachloride is formed even during very slow passage of the chlorine and the presence of a great excess of butadiene in the reaction mixture.
5. The thermal and catalytic isomerization of dichlorobutenes takes place much more slowly than the isomerization of the isomeric alkoxychloropentenes under the same conditions. In the equilibrium mixture, there is 30-33% of the 1,2-dichlorobutene and 67-70% of the 1,4-. The CH_2Cl group has a smaller positive inductive effect than the $ROCH_2 - CH_2$ groups.
6. Addition of chlorine to butadiene takes place, apparently, not only ionically, but in molecular fashion as well; in this latter mechanism, the polarization of the chlorine atom bonds at the moment of addition does not reach the point of ionization.
7. The action of potassium acetate on the isomeric dichlorobutenes gives a mixture of acetates, very close in composition to that formed from the methoxychloropentenes. The 1,4-dichlorobutene-2 reacts in great part according to the S_N type and to a small degree according to the S_N type; the 1,2-dichlorobutene

reacts according to the S_N^1 type.

8. The saponification of 1,4-dichlorobutene-2 by an aqueous solution of soda gives a mixture of diols, consisting of 76% of butene-2-diol-1,4 and 24% of butene-3-diol-1,2. Under similar and more severe conditions, the 1,2-dichlorobutene is not saponified. An explanation of this phenomenon has been given from the point of view of resonance theory.

9. The action of KOH on 1,4-dichlorobutene-2 in a solution of different alcohols gives, in addition to the corresponding diethers, α -chlorobutadiene. The amount of α -chlorobutadiene is increased in the passage from n-propyl to n-butyl, and especially to tert. butyl alcohol. In the latter case, the formation of α -chlorobutadiene becomes the chief reaction. An explanation of the mechanism of reaction is given from the point of view of electron theory.

The action of KOH on 1,2-dichlorobutene-3 both in the absence of a solvent and in solutions of different alcohols, in all cases gives chloroprene only.

10. The action of sodium diethylphosphite and the complete ethyl ester of phosphorous acid on 1,4-dichlorobutene-2 gives 1,2-di-diethylphosphonebutene-2.

The action of the same reagents on 1,2-dichlorobutene-3 did not lead to the isolation of definite products.

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Received March 13, 1948.

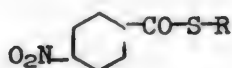
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SYNTHESIS OF THE THIOESTERS OF p-NITROTHIOBENZOIC ACID

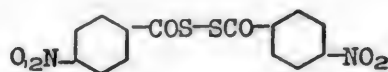
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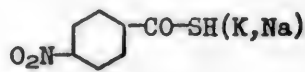
In 1942, Meiser and Schonhofer [1] reported their discovery of a new class of chemotherapeutic substances, represented by the thioesters of p-nitrobenzoic acid (I). At the same time, they showed that 4,4'-dinitrodibenzoyldisulfide (II).



(I)



(II)



(III)

had a chemotherapeutic effect in the treatment of mice inoculated with pneumonia. Unfortunately, the authors did not indicate what sort of thio esters they had utilized for the treatment of their experimental animals; they indicated only that substitution of the nitro group by nitroso, hydroxylamino, azo, and amino groups did not lead to the desired results, nor did the substitution of the

O
 $-\text{C}-\text{SR}$ group by $-\text{C}-\text{NH}_2$, urethane, or others. It was therefore of interest to synthesize both the 4,4'-dinitrodibenzoyldisulfide, as well as the esters of p-nitrothiobenzoic acid. The 4,4'-dinitrodibenzoyldisulfide that we synthesized, the methyl and ethyl esters of p-nitrothiobenzoic acid, and also the potassium and sodium salts of p-nitrothiobenzoic acid (III) were inert, and only the benzyl ester of p-nitrothiobenzoic acid had activity similar to that of sulfa-pyridine.

The synthesis of 4,4'-dinitrodibenzoyldisulfide (II) was carried out according to the method of Kym [2], by the oxidation of p-nitrothiobenzoic acid with ferric chloride solution, and the acid (III) was obtained by the action of potassium sulfohydrylate on the acid chloride of p-nitrobenzoic acid, with subsequent precipitation of the potassium chloride. We must recall that in the reaction of potassium sulfohydrylate with p-nitrobenzoyl chloride, in addition to the potassium salt of p-nitrothiobenzoic acid, there is formed a quite different substance, which was not more closely studied. The methyl and ethyl esters of p-nitrothiobenzoic acid were synthesized from the potassium salt of p-nitrothiobenzoic acid and methyl iodide or ethyl bromide [3]. The benzyl ester of p-nitrothiobenzoic acid was synthesized from the potassium salt of p-nitrothiobenzoic acid and benzyl chloride.

EXPERIMENTAL

The potassium salt of p-nitrothiobenzoic acid. 5 g of caustic potash was dissolved in the minimal amount of water, 100 g of alcohol was added, and the solution was saturated with hydrogen sulfide. To the alcoholic solution of potassium sulfohydrylate, which was cooled and stirred, there was added a solution of 8 g of p-nitrobenzoyl chloride in benzene. Upon removal of the benzene by evaporation, there separated out yellowish brown crystals of the potassium salt of p-nitrothiobenzoic acid, which, after recrystallization from alcohol, melted at 191-192°;

yield, 4.5 g, or 75% of theory.

p-Nitrothiobenzoic acid (III). 5 g of the potassium salt of p-nitrothiobenzoic acid was dissolved in water, and to the solution was added dilute hydrochloric acid. A pale yellow precipitate of p-nitrothiobenzoic acid separated out. The precipitate was filtered off, washed with water, dried, and purified by reprecipitation with hydrochloric acid. The acid melted at 90-95°; yield, 2.8 g, or 67% of theory.

The sodium salt of p-nitrothiobenzoic acid. The salt was obtained in the same way as the potassium salt of p-nitrothiobenzoic acid, and also by dissolving p-nitrothiobenzoic acid in a 10% solution of caustic soda. 9.15 g of p-nitrothiobenzoic acid were dissolved in 20 g of 10% solution of caustic soda. The pasty mass obtained was dried and recrystallized from hot alcohol. Yield 10 g.

0.2000 g substance: 0.2020 g BaSO₄ (according to Messinger)

0.1860 g substance: 0.1920 g BaSO₄

Found %: S 13.9, 14.2.

C₇H₄O₃NSNa. Calculated %: S 15.6.

p,p-Dinitrodibenzoyldisulfide (II). 4 g of p-nitrothiobenzoic acid was dissolved in alcohol, the solution acidified with dilute hydrochloric acid, and a solution of ferric chloride added drop by drop; a precipitate of the disulfide settled out. This was filtered off, dissolved in acetone, and precipitated with water. Pale yellow leaves were obtained, melting at 182-183°; yield, 2.6 g, or 66% of theory.

The methyl ester of p-nitrothiobenzoic acid. To 22.1 g (0.1 mole) of the potassium salt of p-nitrothiobenzoic acid, dissolved in alcohol, 14.2 g of methyl iodide was added. The reaction mixture was heated on a water bath with a reflux condenser for 30-40 minutes, poured off into a porcelain cup, and cooled with ice. The pasty mass obtained was treated with suction, washed with water to remove potassium iodide (test with AgNO₃), dried, and recrystallized from hot alcohol. M.p. 96-97°. 14.2 g of the methyl ester of p-nitrothiobenzoic acid, or 72% of theory, was obtained. The methyl ester of p-nitrothiobenzoic acid was in the form of light yellow crystals, insoluble in water, easily soluble in alcohol, ether, chloroform, and acetone.

The ethyl ester of p-nitrothiobenzoic acid. To the hot alcoholic solution of 22.1 g of the potassium salt of p-nitrothiobenzoic acid was added 10.9 g of ethyl bromide; the mixture was heated on a water bath with a reflux condenser for 30-40 minutes, and the reaction product was cooled, and dried by suction; it was then recrystallized from absolute alcohol. M.p. 67-68°; yield, 14.6 g, or 69% of theory. The ethyl ester of p-nitrothiobenzoic acid was a yellow powder, insoluble in water; it dissolved well in alcohol upon heating, and also in ether, chloroform, and acetone.

The benzyl ester of p-nitrothiobenzoic acid. To 22.1 g of the potassium salt of p-nitrothiobenzoic acid, dissolved in hot alcohol, there was added 12.6 g of benzyl chloride (b.p. 179°); the reaction took place upon heating on a water bath with a reflux condenser for 30 minutes at 50°. The reaction product was recrystallized from absolute alcohol. M.p. 81-82°; yield 7.2 g, or 51% of theory. The benzyl ether of p-nitrothiobenzoic acid was a light yellow powder, insoluble in water, easily soluble in hot alcohol, ether, chloroform, and acetone.

0.4015 g substance: 30.49 g benzene: Δt 0.25°.

0.4590 g substance: 28.48 g benzene: Δt 0.30°.

Found: M 268.7, 273.9.

$C_{14}H_{11}O_3NS$. Calculated: M 273.

0.1906 g substance: 9.10 ml N_2 (16.755 mm).

0.1806 g substance: 8.80 ml N_2 (15.748 mm).

Found %: N 5.5, 5.56.

$C_{14}H_{11}O_3NS$. Calculated %: N 5.3.

0.1903 g substance: 0.1510 g $BaSO_4$.

0.1813 g substance: 0.1414 g $BaSO_4$.

Found %: S 10.9, 10.7.

$C_{14}H_{11}O_3NS$. Calculated %: S 11.7.

SUMMARY

The synthesis of the benzyl ester of p-nitrothiobenzoic acid has been studied, and the syntheses of the methyl and ethyl esters of p-nitrothiobenzoic acid, and of 4,4'-dinitrodibenzoyldisulfide, have been verified.

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Received March 16, 1948.

